VOL. I. NOVEMBER, 1913 NO. 5

AMERICAN CHEMICAL JOURNAL

A QUANTITATIVE STUDY OF ABSORPTION SPECTRA BY MEANS OF THE RADIOMICROMETER

BY J. SAM GUY AND HARRY C. JONES

(This is a continuation of the investigation which has been in progress in this laboratory for the past eight years on the absorption spectra of solutions, aided by grants generously awarded by the Carnegie Institution of Washington to H. C. Jones. This paper contains Chapter VI of Publication of the Carnegie Institution of Washington No. 190.)

The earlier work on the absorption spectra of solutions carried out in this laboratory by Jones and Uhler,[1] Jones and Anderson,[2] and Jones and Strong,[3] in connection with the nature of solution, has been briefly reviewed.[4]

A very small part of the more recent results obtained by Jones and Strong[5] has also been discussed.[6]

[1] Carnegie Institution of Washington, Publication No. **60**; THIS JOURNAL, **37**, 126, 207 (1907).

[2] Carnegie Institution of Washington, Publication No. **110**; THIS JOURNAL, **41**, 163, 276 (1909).

[3] Carnegie Institution of Washington, Publication No. **130**; THIS JOURNAL, **43**, 37, 97, 224 (1910).

[4] Z. physik. Chem., **74**, 325 (1910).

[5] Carnegie Institution of Washington, Publication No. **180**; THIS JOURNAL, **45**, 1, 36, 113 (1911); **47**, 27, 126 (1912).

[6] Z. physik. Chem., **80**, 361 (1912).

We[1] have extended the work of Jones and Strong on the absorption spectra of solutions at high temperatures. The closed apparatus devised by Jones and Strong was used. It consisted of a gold-plated brass tube, closed at the ends by glass windows, and these were held in place by suitable screw heads. The absorption spectra of a fairly large number of aqueous solutions were studied up to 200°. The absorption bands of salts of neodymium become more diffuse with rise in temperature. The two bands λ4275 and λ5800 widen rapidly with rise in temperature, the widening being almost entirely towards the longer wave lengths. The absorption spectra of salts of praseodymium were only slightly affected by change in temperature. In the more concentrated solutions all of the bands are slightly widened, there being no appreciable change in the more dilute solutions. The absorption bands of uranyl salts nearly all widened with rise in temperature, the widening being especially pronounced towards the red. Several bands had their centers shifted as much as 15 Å. U. towards the red.

We also studied the effect of dilution on the absorption spectra of solutions. The earlier work of Jones and Anderson and Jones and Strong had shown that if dilution has any effect on the absorption spectra of solutions, it is in many cases very slight. Especially devised apparatus must, therefore, be constructed to test this effect.

The most concentrated solution used was placed in a cell whose depth was 0.5 cm. This solution was then diluted one hundred times and placed in a cell whose depth was 50 cm. The second solution was then diluted five times, and the light sent through a layer whose length was 250 cm. In this way a constant amount of absorbing matter was, in all three cases, kept in the path of the beam of light. The dissociation of the most concentrated solution was greatly increased with an increase in dilution of five hundred times. By comparing the spectrograms for the three concentrations of any given substance, we could see what effect increase in ionization or increase in hydration had on the absorption spectra.

[1] Carnegie Institution of Washington, Publication No. **190**; THIS JOURNAL, **49**, 1 (1913).

The neodymium band, λ5800, widened about 60 Å. U. in the most concentrated solution, the widening being towards the red end of the spectrum. The widening of the double band λ5150 is symmetrical towards both ends of the spectrum.

Rise in temperature and concentrating the solution produce the same effect on bands λ4275 and λ5800. These bands are widened. Band λ5100 is changed by dilution but not by temperature. This would indicate that this band was due to molecules, which, with dilution, are broken down into ions. The bands λ4275 and λ5800, being affected in the same way by temperature and concentration, probably have to do with the hydrated molecules, since both of these influences would simplify the hydrates.

The λ5100 band is not appreciably affected by temperature, but is affected by change in dilution. This band is widest in the most concentrated solution. Since temperature has little or no effect on this band, hydration can have nothing to do with it. This band, widening as the number of molecules is increased, would indicate that it was produced by the unhydrated molecules. The remaining neodymium bands are affected neither by temperature nor dilution. They are, therefore, associated with the atoms or ions.

THE RADIOMICROMETER

The radiomicrometer used in this work consisted of a loop of thin copper wire suspended in a magnetic field. The greatest difficulty in building the radiomicrometer was to secure copper wire free from magnetic metals. If the copper contained magnetic impurities there resulted a "magnetic control" which destroyed the sensitiveness of the instrument. The best copper wire was secured from Leeds & Northrup, of Philadelphia, and from R. W. Paul, of London. The outside of the wire was dissolved away in nitric acid, to remove any iron adhering from the die in which the wire was drawn.

The alloys used in making the thermoelectric junction consisted, the one of ninety parts bismuth and ten parts tin, and the other of ninety-seven parts bismuth and three parts anti-

mony. The method of soldering the alloys to one another and to the loop of copper wire we owe to Professor A. H. Pfund.[1] A light glass rod was attached to the end of the loop of copper wire opposite the thermal junction. This carries the mirror and the whole is suspended by means of a quartz fiber. The entire system weighed about 20 mg. and was so suspended that the loop of copper wire hung between the poles of a strong magnet. The entire system was suspended in a glass tube closed at the top by a ground-glass stopper and provided with suitable windows for exposing the junction and observing the mirror. The ground-glass stopper, from which the whole system was suspended, could be turned and the loop made to occupy any desired position relative to the magnet. The whole apparatus was packed in cotton, only the junction being exposed to the radiation.

The radiomicrometer which we built had a whole period of eight seconds. A candle placed at a distance of a meter gave a deflection of *15* cm., the light being allowed to fall on the thermal junction after passing through a glass window. When this radiomicrometer was suspended in a vacuum a candle at a distance of a meter gave a deflection of 50 cm. Since glass absorbs about half of the energy emitted by a candle, if our radiomicrometer had been provided with a rock-salt window and exhausted, a candle placed at a distance of a meter would give a deflection of *100* cm.

The "magnetic control," due to traces of magnetic impurities in the best copper wire, was, of course, greater the more sensitive the instrument. We, therefore, did not use our radiomicrometer in a vacuum. The quartz fiber was so chosen that a candle at a meter distance gave a deflection of 16 cm. The instrument had a whole period of 8 seconds, and this was sufficient sensibility for all wave lengths greater than $\lambda 4500$. The measurements could thus be quickly made, and the magnetic disturbance was negligible.

When the source of the energy was removed the instrument returned to its original zero to within 0.5 mm. Repeated readings agreed to within one per cent. The source of energy

[1] Physic. Rev., **34**, 228 (1912); Physik. Z., **13**, 870 (1912).

was a Nernst glower, attached to a storage battery, having a voltage of 110 and an amperage of 1.2. This was found to be very constant. An ammeter was, however, kept in the circuit.

The details of the manipulation have already been described.[1] The light, after passing through the solution and the slit of the spectroscope, fell upon the prism of the Hilger spectroscope. A second slit was inserted in the spectroscope instead of the eye-piece. The light passed from the prism through this second slit, and was then focused on the thermal junction of the radiomicrometer. The Hilger spectroscope contained a milled head, graduated so that the wave lengths could be read off directly. By suitably turning this head any desired wave length could be thrown upon the junction of the radiomicrometer.

The first problem that was studied by means of the radiomicrometer was the *effect of dilution* on the absorption spectra of solutions. The concentration of the solution was varied, and the depth of layer of the solution through which the light passed was varied to the same extent, so that the concentration, n, times the depth of layer, d, remains constant:

$$nd = \text{constant}$$

If the solvent plays no role in the absorption of light, the absorption curves for the different concentrations of any given substance must fall directly over one another, since the number of absorbers in the path of the beam of light is kept constant.

An examination of the transmission curves for neodymium chloride shows that the more concentrated the solution the less the transparency and the *broader* the absorption bands. In the more dilute solution the *intensity* of the bands is, however, greater; and with increase in dilution the middle of the band is displaced towards the region of greater wave length.

Similar relations were found for neodymium bromide and neodymium nitrate; with increasing dilution the intensities of the bands increase, and the centers are displaced somewhat towards the longer wave length. Neodymium sulphate

[1] Physik. Z., **13**, 649 (1912); THIS JOURNAL, **49**, 31 (1913).

and acetate were also studied by means of the radiomicrometer. The absorption of the acetate is much greater than that of any other neodymium salt thus far studied, which agrees with the results obtained earlier by means of the grating spectroscope and the photographic plate.

The advantage of the radiomicrometer over the grating spectroscope is that it enables us to measure not only the positions of the bands, but their intensities and the different intensities of different parts of the same band. It further enables us to work over a much greater range of wave lengths. The photographic plate is sensitive only as far as λ7600, while the radiomicrometer can be used to λ20000 or even to λ30000.

THE ABSORPTION OF LIGHT BY COMBINED WATER DIFFERENT FROM THAT OF FREE WATER

The second problem which was attacked by the radiomicrometric method is indicated by the above heading.[1] The absorption spectra of a large number of salts of different metals were being studied at the beginning of the present academic year. These spectra were compared with the absorption of water, using the same depths of water as the water in the various solutions. The depth of water in the solution was determined from its concentration and its specific gravity. It was found that the absorption of the solution was *less* than that of a layer of water having a depth equal to the depth of the water in the solution. This observation at first surprised us. We had assumed up to this time that in an aqueous solution the water present absorbed just as much as an equal layer of pure, uncombined water. The above observation showed that this assumption was absolutely wrong. We could now no longer measure the absorption of a solution, subtract the absorption of water and conclude that the remainder was the absorption due to the dissolved substance, since the water in the solution has different absorption from an equal thickness of pure, uncombined water.

We then studied the absorption spectra of a number of substances, in cells whose depths could be easily and accurately

[1] THIS JOURNAL, **49**, 265 (1913).

adjusted. We then measured the absorption spectra of water having the same depths of layer as the water in the solutions. We found that for certain substances the pure water was more opaque than the solutions, and for other substances the water was more transparent.

It was soon noted that solutions of those substances which are *largely hydrated* are more transparent than pure water having the depths of the water in the solution. Aqueous solutions of *nonhydrated* or only *slightly hydrated substances*, provided the substances themselves do not absorb light, are not more transparent than pure water having the same depths as the water in the solution. This would indicate that *water combined with the dissolved substance had less absorption of light than pure, uncombined water.*

The object of the second line of work with the radiomicrometer was to test this point. The details of this work have already been published. For these, reference must be had to the earlier publications.[1]

An examination of the results for potassium chloride, ammonium chloride and ammonium nitrate, i. e., for those substances which combine with very little water, shows that for all of the wave lengths studied, the solution and water of the same depth as the water in the solution have practically the same transmission. The dissolved substance does not combine with the solvent water, and the water in the solution has almost exactly the same effect upon light as so much pure water would have. This is exactly what would be expected from our knowledge of the absorption of light by dissolved substances and by the solvent.

The results for calcium chloride, magnesium chloride and aluminium sulphate, i. e., for salts which, in aqueous solution, are strongly hydrated, show that the *solution is often more transparent than the same amount of water that is contained in the solution.*

The greater transparency of the solution as compared with the water in the solution must be due to some action of the

[1] Physik. Z., **14**, 278 (1913); THIS JOURNAL, **49**, 265 (1913); Chem. News, **108**, 25, 37 (1913).

dissolved substance on the solvent water. The important question is, what is this action?

Our earlier work on the absorption spectra of solutions has shown that the solvent can have a marked effect on the power of the dissolved substance to absorb light. This was first demonstrated by Jones and Anderson,[1] who found that neodymium chloride dissolved in water had very different absorption from neodymium chloride dissolved in methyl alcohol. A large number of examples, illustrating the same point, have since been found by Jones and Strong.[2] We interpreted the effect of the solvent on the power of the dissolved substance to absorb light as due to a combination between a part of the liquid present and the dissolved substance. This enabled us to explain a large number of facts that were brought to light by the investigations that have been carried on in this laboratory, and which do not seem to admit of any other explanation. In a word, the solvate theory of solution, as proposed by Jones[3] fourteen years ago to supplement the theory of electrolytic dissociation in order that we might have a theory of the real solutions that we use in the laboratory, and not simply a theory of ideal solutions, as the theory of electrolytic dissociation alone must be regarded, has served a good purpose in explaining the phenomena that have been previously observed in connection with the absorption of light by solutions.

We are inclined to explain the phenomena recorded in this paper by means of the same theory. For solutions of those substances which have been shown by entirely different methods not to hydrate to any appreciable extent, the absorption of light by the solution and by a layer of water equal in depth to that of the water in the solution is, to within almost the limit of experimental error, the same.

For those substances which have been shown to form complex hydrates, however, the absorption of light by their solu-

[1] Z. physik. Chem., **74**, 359 (1910); Carnegie Institution of Washington, Publication No. **110**.

[2] Carnegie Institution of Washington, Publications Nos. **130** and **160**; Z. physik. Chem., **74**, 68 (1910); **80**, 361 (1912).

[3] THIS JOURNAL, **23**, 89 (1900).

tions and by a layer of water equal in depth to that of the water in the solution is very different. The water in these solutions is usually more opaque to light than the solution, or, what is the same thing in other words, a solution is more transparent than the water that is present in the solution.

The most rational explanation of this phenomenon appears to us to be that the part of the water that is combined with the dissolved substance has a smaller power to absorb light than pure, free, uncombined water. The fact that we are able to detect the difference between the water in the solution and pure water, by its action on light, we regard as good evidence in favor of the water in the solution being different from pure, free water. This difference, it seems to us, can be readily accounted for by the fact that a part of the water present in the solution is in combination with the dissolved substance.

ABSORPTION SPECTRA OF A NUMBER OF SALTS AS MEASURED BY MEANS OF THE RADIOMICROMETER

The results already published, which are concerned with the energy measurements of the absorption spectra of solutions by means of the radiomicrometer, were obtained by comparing the intensity of a given source of light (after passing through the solution) with the intensity of the same source of light after passing through an equal depth of water. In a word, the depths of cells in each case were the same. As has already been stated, a cell whose depth was 1 cm. was filled with the solution and placed in the path of the beam of light and the deflection of the instrument noted; then a cell of the same depth was filled with the solvent and interposed in exactly the same position as the former cell, and the deflection of the instrument again noted. Denoting the former by I and the latter by I_o we get the ratio I/I_o, which represents the percentage transmission of the solution as compared with water. Such a procedure was repeated at frequent intervals throughout the spectrum, locating a series of points through which the transmission curves could be drawn.

Certain phenomena presented themselves throughout the course of this investigation, which suggested a more careful

study of some of the absorption bands located in the infrared portion of the spectrum; and at the same time it was thought advisable to map the absorption spectra of some of the more common salts of cobalt, nickel, etc., in terms of Beer's law, since up to the time of this investigation no quantitative study of the infrared spectrum of these salts had appeared.

In order to make a careful study of the exact intensity of the various portions of any given bands, it is clear that we are dealing with a much more complex and intricate problem than simply with the location of the band; and on this account it was necessary to improve our apparatus and at the same time to exert more care, if possible, in carrying out any given operation.

It was early found that if we desired to study that region of the infrared spectrum in which water had considerable absorption, we must not compare our solutions with an equal depth of layer of water, as noted above, but with a depth of layer equal to the water in the solution, which in the most concentrated solutions was much less than the actual depth of the cell containing the solution—a part of the cell's depth being occupied by the dissolved substance. Even when such a correction was made, it was found that for a given wave length in the water absorption bands, the solution gave greater deflections than did the solvent, i. e., that in such regions the solution was actually more transparent than an equivalent depth of water.

Remembering that the solutions with which we were then working, i. e., solutions of salts of neodymium and praseodymium, were strongly hydrated, it was thought that in view of the fact that at least a part, and in the concentrated solutions a considerable part, of the water present was there as water of hydration, it would be advisable to study the effect of colorless hydrated salts upon the absorption of water.

This chapter of our work has been sufficiently discussed elsewhere, and will be taken up here only to state that these experiments showed clearly that there were many variables to be considered. We have, first, the effect of the solvent on the absorption of the solute; and, secondly, the effect of the solute

upon the absorption of the solvent. In addition to these, there was, of course, the absorption of the solvent and the solute independently. Such being the case, we would not be obtaining comparable results for various dilutions of any solutions in terms of Beer's law, even if we did compare each dilution with an equivalent amount of water. It is clear that by so doing we would not be getting comparable ratios, since the solvent and the solute were mutually affecting each other's absorption; and this effect would not be the same for the different dilutions of the same salt.

Mode of Procedure

It is, however, possible to get the exact transmission of a given depth of solution by a method of differentiation. If we placed in cell A 11 mm. of a solution and in cell B 1 mm. of the same solution, the ratio representing the respective deflections of the instrument, when these cells are alternately placed in the path of the beam of light, should give the absorption or transmission of (11 — 1) or 10 mm. of the solution.

Since, if we let A be the percentage absorption of a unit's depth of layer of the solution, and I_o the initial intensity of the light impinging upon the surface of the source, we get:

AI_o = amount of light absorbed by first unit layer of the solution. Then,

$I_o - I_oA = I_o(1 - A)$ = light incident upon surface of second unit layer.

Denoting this by I_1, we get

$$I_1 = I_o - I_oA = I_o(1 - A) \text{ or } I_1/I_o = 1 - A$$

Considering again the third unit layer, we get, by similar reasoning,

$I_1 - I_1A$ = amount of light incident upon its surface.

Denoting this by I_2 we get

$$I_2 = I_1 - I_1A = I_1(1 - A)$$

but $I_1 = I_o(1 - A)$; therefore, $I_2 = I_o(1 - A)^2$; hence $I_n = I_o(1 - A)^n$.

We can then, by this process, obtain transmissions for given depths of solutions and for varying concentrations. This was the method adopted throughout this chapter of the work.

Description of Cells Used

In all cases where we were dealing with different depths of layer, it was necessary to use cells adjustable in length. A very satisfactory form of cell was devised and used throughout the latter part of this work. It consisted essentially of two brass cylinders telescoping neatly into each other. The external diameter of the outside cylinder was about 2.5 inches, and the thickness of the walls was in every case about 2 mm., which was sufficient to withstand handling without danger of changing the shape of the cell.

Into the ends of each cylinder there was sealed, by means of Wood's metal, a glass plate about 1 mm. thick and made of the very best optical glass. In all cases the glass plates were so nearly parallel that they showed interference fringes; and both cells gave the same deflections, either when empty or filled with the same solution and placed in the path of the light before the radiomicrometer.

After adjusting the glass ends and fixing them securely by means of Wood's metal, the entire cell was first plated with silver, being taken out of the plating bath from time to time and polished to a bright surface with the finest crocus paper. On top of this silver coating a heavy plating of gold was deposited. The distance between the glass plates fastened to the ends of the telescoping cylinders, which determined the depth of layer of solution used, was in all cases fixed by gold-plated washers, whose thickness had been accurately measured to 0.001 inch by means of a vernier caliper.

Before any series of readings was made, the positions of the two cells were so adjusted in the sliding carriage as to give equal deflections, when alternately placed in the same position before the radiomicrometer, in that portion of the spectrum where neither the solute nor solvent had any absorption; and from time to time throughout the experiment duplicate readings were made on this point to see that the cells had not changed their relative positions. In case any change was noted, a duplicate series of readings was always made. Such readings upon the same cell usually agreed to about one division of the scale, which corresponded to about 1 to 2

per cent., depending upon the throw of the instrument. In the midst of the very intense absorption bands, where the deflections of the instrument were small, reaching zero at many points, the error resulting from any drift in the instrument of reading of the scale was greater than the mean error given above.

In nearly all cases new solutions were made up and the results duplicated, so that the tables and curves below represent a mean of several series of readings. In most cases the agreement was very satisfactory, usually the difference not being over 3 per cent.

Since any change in the position of the prism was a determining factor in the portion of the spectrum which fell upon the thermo-junction, and since in the very intense, sharp bands of the neodymium salts any slight change in the position of the prism would make a great difference in the final results, great care had to be exerted in setting the head reading of the spectroscope. A change of one division on the calibrated head, which in the longer wave lengths was only about 2 mm., often made a change of 100 per cent. in the scale reading. Such difficulties were not met with in solutions where the absorption bands were broad and diffuse, as in salts of cobalt, nickel, etc.

In studying the changes which might occur in any band, it is of course necessary that all conditions be as nearly as possible the same. One of the most important factors here is that of the width of the slits of the spectroscope. With those solutions whose absorption bands are broad and diffuse, not having such well-defined edges as with the salts of neodymium and praseodymium, this is not such a determining factor. Should the band be very narrow—say approaching that of the width of the slit necessary to be used in order to secure reasonable deflections of the instrument—it is seen that any slight change in the slit will make a large difference in the amount of light falling on the thermal junction.

Considering a concrete example, let us suppose that the slit width is just equal to that of the absorption band, under a given dispersion. If, now, the band and the slit exactly coin-

cide, it is evident that no light will be falling upon the junction, this being indicated by zero deflection of the instrument. If, on the other hand, the slit is slightly wider than the band, some light will enter around the edges of the band; and, although the narrow band may actually have complete absorption at a given point, it would not be indicated by the instrument, since some light is entering around the edges of the band.

Denoting the deflection of the instrument for a cell of 2 mm. depth of a solution of x concentration by A, and the same for 1 mm. of the same solution by B, we get, by the differential method discussed above, the ratio A/B for the intensity of the light transmitted by $(2 - 1)$ or 1 mm. of the solution in question.

By a similar reasoning we get the ratio A'/B' for the value of the transmission of a solution of concentration $x/20$, using absorbing layers 21 mm. and 1 mm., respectively. While such a method is theoretically and mathematically correct for infinitely narrow slit widths, and practically so for bands which are wide in comparison with the necessary slit widths, yet, in the case of very sharp, narrow neodymium bands it has been found not to give comparable results. The reason for this is clearly seen in the light of the facts discussed above.

Let us consider the ratios A/B and A'/B'. In the first case we are dealing with concentrated solutions, where the absorption bands are broad; hence B is small, and, in case the slit width is comparable with the width of the absorption band, B will be very much smaller than B', since B' is only 1 mm. of an $x/20$ concentration solution. In a word, B, which is 1 mm. of the more concentrated solution, has 20 times as many absorbers as has an equal depth represented by B', and a decrease in the denominator of the fraction means an increase in its value.

While the ratios A/B and A'/B' give the transmissions for 1 mm. of a solution of concentration x, and 20 mm. of a solution of concentration $x/20$, respectively, provided the slits are narrow, yet in the visible part of the spectrum, where such

wide slits had to be used on account of the small amounts of energy in this region, these ratios are not comparable.

For this reason we have confined the larger part of our work on neodymium compounds almost entirely to wave lengths greater than 0.7μ. In all the following tables and curves representing these data, constant slit widths of 0.2 mm. have been used. This was the minimum width which could be employed in order to get reasonable deflections throughout the spectrum from 0.7μ to 1μ. Experiments have shown that any error resulting from slit widths would not amount to more than 3 or 4 per cent. throughout this region.

The source of light was, as in the previous work, a Nernst glower carrying about 1.2 amperes, and the current was kept constant by means of an adjustable slide-wire resistance. The source of current was a large number of storage cells, and this was never allowed to vary over 0.01 ampere. Great care was exerted in keeping the current constant while obtaining a single ratio, since this is really the only time in which a slight change in current density was dangerous.

DISCUSSION OF TABLES AND CURVES

Neodymium Chloride in Water

Table I gives the observed transmissions of solutions of neodymium chloride in water. In all the tables the following four dilutions have been studied, the depths of cell being, generally, 2.5, 5, 10, and 20 mm, respectively, and the concentrations being made so as to keep $n \times d = k$. In column 1 of each table there is given λ, taken at such intervals as the solution in question required. In those portions of the spectrum where the transmission was complete, or very nearly so, these intervals were greater than in those regions where there were absorption bands.

Reading from left to right in this table, beginning with column 2, there are given the absorptions for solutions of the following concentrations: 2.141, 1.07, 0.535, and 0.267 normal, respectively, the corresponding depths of absorbing layer being 2.5, 5, 10 and 20 mm., respectively. In every

case the transmission was obtained from the ratio $(x + 1)/1$, where x is 2.5, 5, 10 and 20 mm., respectively.

In all cases the concentrated mother solution was carefully made up, its concentrations determined by a gravimetric precipitation of the metal, and the succeeding solutions made by diluting measured parts of the mother solution.

Observations are given here over only that portion of the infrared spectrum from λ6800 to λ10000. It is in this region that the most pronounced neodymium bands occur. It was thought advisable not to go further into the infrared, since beyond 1 μ the general absorption due to the solvent is very marked. This would, of course, interfere with a quantitative study of any band occurring in this region, since it is impossible to separate the two absorptions, previous work having shown that they are not additive.

The work in the visible region of the spectrum was limited by the slit widths necessary to be used, which has been mentioned and discussed above. We have rather chosen a limited portion of the infrared, over which we could work without altering either the intensity of the light or the slit width, which was in all cases 0.2 mm.

Table I—Percentage Transmission of Neodymium Chloride Solutions

λ	D. = 2.5 mm. C. = 2.141 N	D. = 5 mm. C. = 1.071 N	D. = 10 mm. C. = 0.535 N	D. = 20 mm. C. = 0.267 N
686	93	88	88	86
693	95	95	95	94
698	96	96	96	94
704	96	96	98	94
708	96	93	95	92
712	92	93	95	88
716	88	89	88	85
720	81	78	81	81
723	64	62	63	56
726	32	31	25	23
730	7	7	5	6
733	0	0	0	0
737	0	0	0	0
741	5	2	1	2
746	18	14	12	5
751	36	39	29	28

755	54	55	52	49
759	75	74	72	68
763	85	85	83	81
767	84	86	85	83
770	79	81	80	76
774	67	73	65	61
779	47	45	45	40
783	29	27	26	24
787	22	10	10	7
791	0	0	0	0
796	0	0	0	0
800	15	10	8	6
805	24	23	22	18
809	40	39	38	37
814	58	58	58	53
819	80	78	78	76
825	89	91	91	82
830	93	92	93	88
834	94	95	95	88
839	93	93	93	87
845	91	92	91	86
850	87	86	87	78
856	75	73	71	66
861	54	46	43	40
867	29	21	18	16
872	28	24	23	18
877	40	39	40	34
882	53	48	52	47
888	60	59	60	53
894	61	59	61	56
900	67	66	66	59
906	80	78	79	71
912	90	92	89	79
917	96	93	94	86
923	98	97	96	86
928	98	96	96	84
933	98	96	96	81
938	98	94	90	75

The curves representing this table are given in Figs. I–IV, inclusive. The percentages of transmission are plotted as ordinates, while the wave lengths are given as abscissas. An examination of these curves shows three pronounced minima, representing the three absorption bands, with their centers

near λ7300, λ7950 and λ8700, and less marked bands near λ7150 and λ9000. The latter of these small bands is possibly

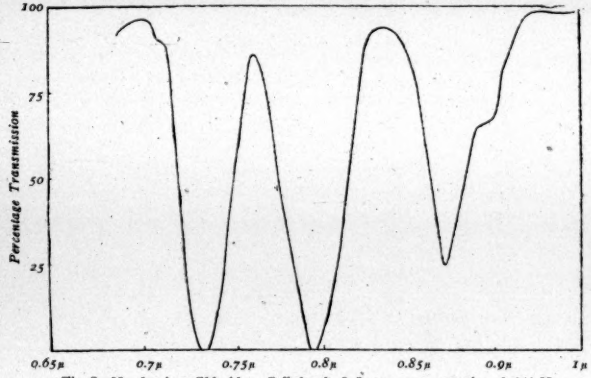

Fig. I—Neodymium Chloride. Cell depth, 2.5 mm.; concentration, 2.141 N

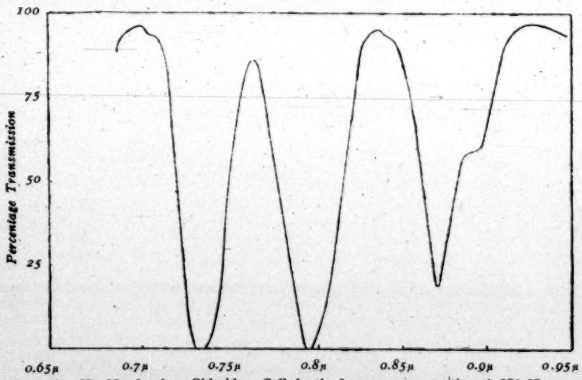

Fig. II—Neodymium Chloride. Cell depth, 5 mm.; concentration, 1.071 N

due in part to the absorption of the solvent; but since its intensity does not increase markedly with dilution, it is more

probably a doublet. Considering the curves representing all four dilutions, we see that the λ7300 and λ7900 bands show complete absorption over a considerable range of wave lengths, and any change in intensity could not be very noticeable. The λ8700 band, however, has its minima gradually lowered as we pass from Fig. I to Fig. IV, i. e., in the direction of increasing dilution. This phenomenon has been noted elsewhere, and a possible explanation of it based upon a theory of resonance suggested. A closer and more exact study has shown that although the phenomenon is a real one, yet it is probable that it may in part be due to the combined effect of the slight water absorption and, even a more important factor, the slit widths, as discussed above.

The regions of maximum transmission occur near λ7600 and λ8400, and solutions of neodymium chloride become almost completely transparent beyond 1 μ, except for the general absorption of the solvent. Slight absorption bands occur in this region, one near 1.5 μ, but they are so masked by the intense water absorption that it was found impossible to make a quantitative study of them.

From a comprehensive study of the four curves representing the absorption spectra of concentrated solutions of neodymium chloride, it seems probable that Beer's law holds quantitatively for the infrared region, except for such slight changes as have been fully discussed above.

Since, as mentioned above, the absorption bands with their centers near λ7300 and λ7950, in solutions of such concentrations as are given in Table II, reach complete absorption, and as in such cases it would not be easy to detect any change in their intensity, it was thought advisable to make a study of a series of more dilute solutions of the same salt.

The results of this experiment are given in Table II. Reading from left to right, the concentrations are 0.536, 0.267, 0.133, and 0.067 normal, respectively, the corresponding depths of absorbing layers being 2.5, 5, 10, and 20 mm., respectively. Here again it is seen that the conditions of Beer's law are adhered to. The results are graphically represented in Figs. V to IX, inclusive. These curves show minima in

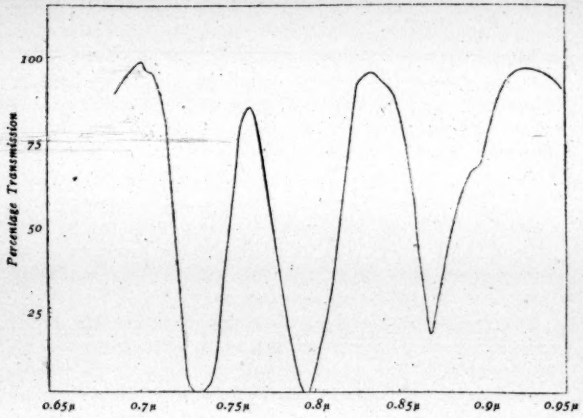

Fig. III—Neodymium Chloride. Cell depth, 10 mm.; concentration, 0.535 N

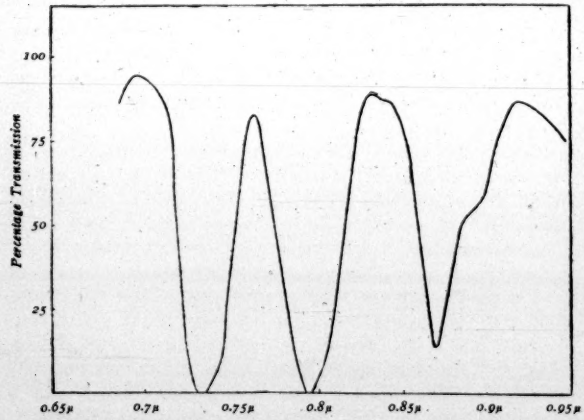

Fig. IV—Neodymium Chloride. Cell depth, 20 mm.; concentration, 0.267 N

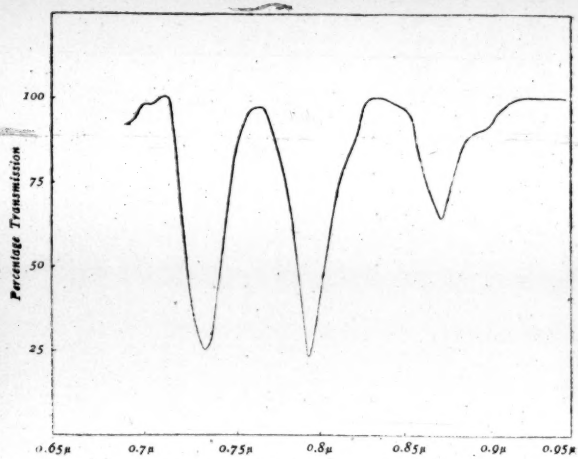

Fig. V—Neodymium Chloride. Cell depth, 2.5 mm.; concentration, 0.536 N

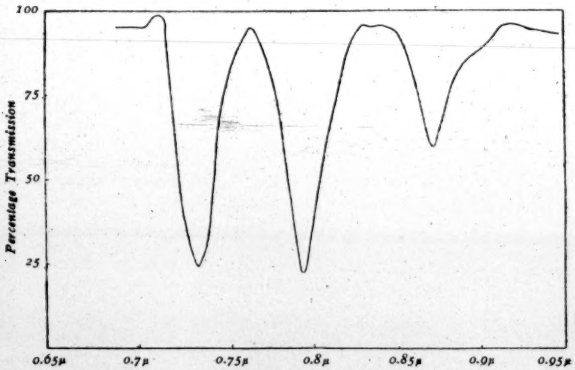

Fig. VI—Neodymium Chloride. Cell depth, 5 mm.; concentration, 0.267 N

about the same positions as did the curves representing the mere concentrated solutions, but since the solutions are more dilute, they are accordingly more transparent; hence the minima in the curves are not so pronounced. The maxima occurring near λ7300 and λ7900 are at about 25 per cent.

Table II—Transmission of Neodymium Chloride Solutions (Dilute)

λ	D. = 2.5 mm. C. = 0.536 N	D. = 5 mm. C. = 0.267 N	D. = 10 mm. C. = 0.133 N	D. = 20 mm. C. = 0.067 N
686	92	95	94	92
693	93	95	95	97
698	97	95	95	97
704	98	95	96	97
708	98	95	97	98
712	100	98	96	96
716	100	98	98	92
720	96	94	89	89
723	85	84	83	84
726	59	54	58	53
730	42	41	40	34
733	31	29	26	25
737	25	24	20	22
741	28	29	29	29
746	47	44	51	44
751	69	65	65	60
755	85	82	82	78
759	93	86	90	86
763	97	90	92	92
767	97	95	90	92
770	97	93	90	89
774	91	86	87	84
779	79	76	78	74
783	69	61	59	56
787	47	39	38	34
791	23	24	20	18
796	28	25	23	23
800	45	39	38	39
805	64	59	57	57
809	78	72	71	70
814	85	84	82	82
819	92	91	88	88
825	100	94	94	94
830	100	96	94	93
834	100	94	94	92

839	100	96	93	91
845	98	95	94	91
850	97	94	90	89
856	92	87	84	83
861	78	77	74	70
867	70	64	62	60
872	64	60	59	56
877	74	71	68	66
882	84	80	76	75
888	89	84	82	78
894	90	84	83	79
900	91	88	86	81
906	95	90	87	83
912	98	95	90	84
917	100	96	92	85
923	100	96	93	84
928	100	95	92	84
933	100	94	94	83
938	100	94	95	78

Table III—Transmission of Neodymium Nitrate Solutions

λ	D. = 2.5 mm. C. = 2.010 N	D. = 5 mm. C. = 0.15 N	D. = 10 mm. C. = 0.525 N	D. = 20 mm. C. = 0.262 N
686	86	88	85	78
693	93	96	91	89
698	93	96	93	93
704	96	94	93	91
708	95	96	96	88
712	89	90	94	89
716	84	88	88	82
720	78	79	78	78
723	80	63	61	58
726	40	33	30	28
730	14	14	10	9
733	0	0	0	0
737	0	0	0	0
741	11	4	0	0
746	12	15	6	6
751	22	23	22	17
755	38	39	40	38
759	60	60	62	55
763	75	75	74	70
767	80	80	83	79
770	75	75	79	75
774	64	66	68	62
779	47	47	48	44

(*Table III continued.*)

λ	D. = 2.5 mm. C. = 2.010 N	D. = 5 mm. C. = 0.15 N	D. = 10 mm. C. = 0.525 N	D. = 20 mm. C. = 0.262 N
783	32	32	29	26
787	16	10	13	9
791	11	8	2	5
796	0	0	0	0
800	12	10	6	6
805	21	19	14	15
809	35	33	30	30
814	49	49	47	47
819	63	67	65	64
825	79	80	79	77
830	82	88	89	82
834	92	92	93	85
939	96	94	94	89
845	92	91	91	85
850	87	84	85	77
856	76	70	72	65
861	61	57	53	47
867	43	36	35	32
872	30	27	26	22
877	31	30	28	25
882	43	42	41	36
888	55	52	51	48
894	65	60	59	61
900	68	66	66	62
906	77	75	75	67
912	86	84	83	75
917	94	90	97	83
923	98	92	90	84
933	100	96	88	86
938	100	96	83	77

The λ8700 band has a minimum transmission in regions λ7200, λ7600, λ8300 and λ9300. It will be noticed that beyond 0.9 μ all of the curves drop sharply with dilution, which is due entirely to the increasing absorption of the water.

Curves V to IX, inclusive, show just what might be anticipated from Curves I to IV, a lowering of absorption maxima as we pass towards the more dilute solutions. This change is most marked in the λ8700 band, and it is in this region that the absorption of the water is most pronounced, although a 20 mm. layer of water in this region has at no point over 10

per cent. absorption. The change in the intensity of the absorption band is greater than this amount, but it seems proba-

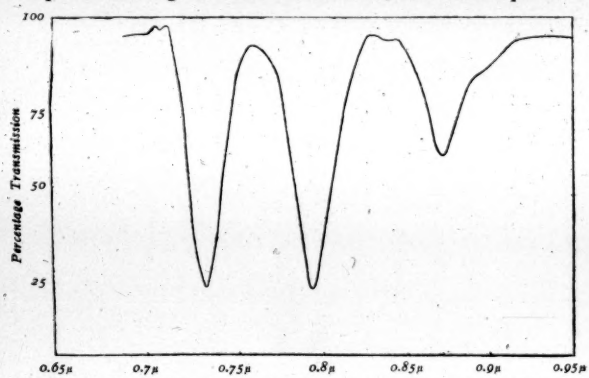

Fig. VII—Neodymium Chloride. Cell depth, 10 mm.; concentration, 0.133 N

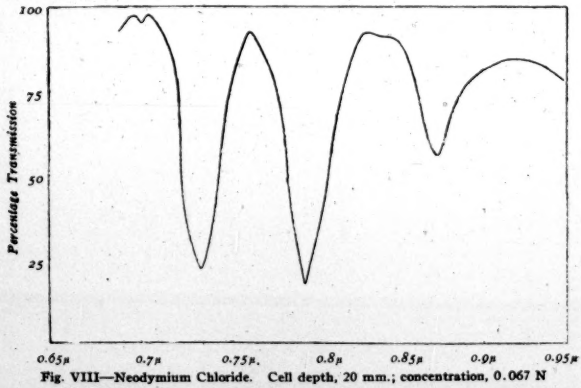

Fig. VIII—Neodymium Chloride. Cell depth, 20 mm.; concentration, 0.067 N

ble that this, together with the added correction for the slit widths, may account for the phenomenon, and that Beer's law holds for the dilute solutions of neodymium chloride.

Neodymium Nitrate

Table III gives the percentage transmission for solutions of neodymium nitrate. Column 1 gives the respective wave

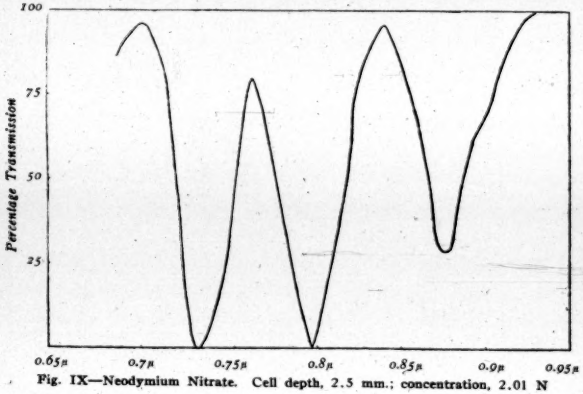

Fig. IX—Neodymium Nitrate. Cell depth, 2.5 mm.; concentration, 2.01 N

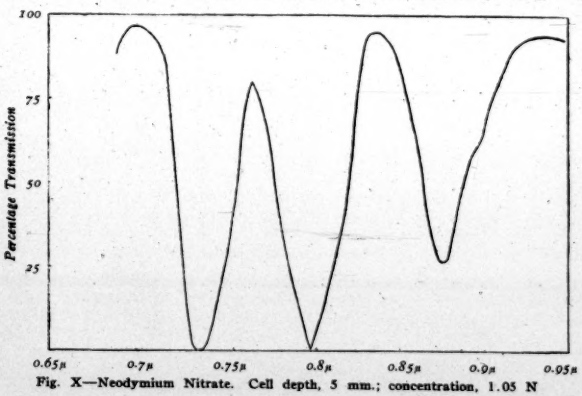

Fig. X—Neodymium Nitrate. Cell depth, 5 mm.; concentration, 1.05 N

lengths at such intervals as the solutions required. Reading from left to right, we find the percentage transmissions for the

following concentrations: 2.010, 1.050, 0.525, and 0.262 normal, respectively, the corresponding depths of absorbing

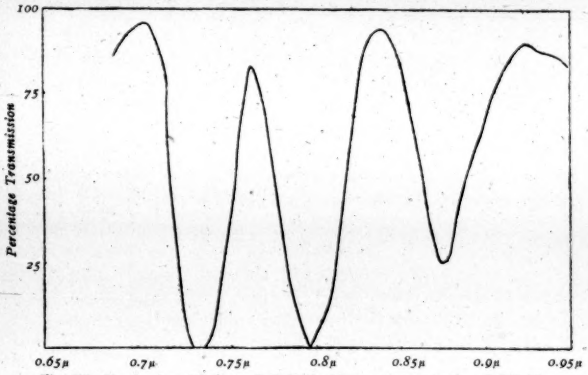

Fig. XI—Neodymium Nitrate. Cell depth, 10 mm.; concentration, 0.525 N

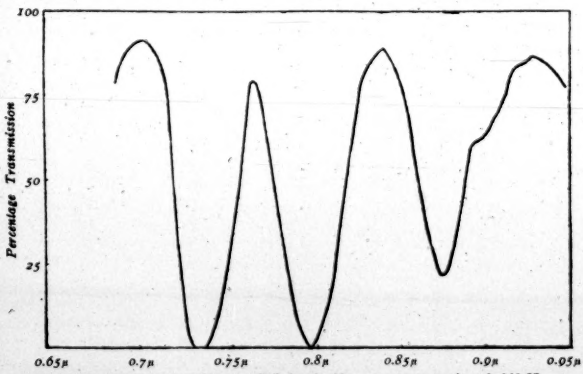

Fig. XII—Neodymium Nitrate. Cell depth, 20 mm.; concentration, 0.262 N

layers being 2.5, 5, 10, and 20 mm. Curves IX to XII, inclusive, represent these results, the abscissas being wave

lengths and the percentage transmissions being given as ordinates. It is seen that the absorption bands in the nitrate solutions, as with those of the chloride discussed above, show three minima at λ7300, λ7950 and λ8750. The nitrate bands are not as intense as those of the concentrated solutions of the chloride given in Curves I to IV. This is what we should expect, since the concentrations of the nitrate solutions are not so great. However, two of the absorption bands reach zero transmission. A comparative study of any of these bands in the succeeding curves shows that, just as was found with the chloride bands, they become more intense with dilution. The decided decrease in the transmission in the regions of the spectrum beyond 1μ is undoubtedly due to the increasing absorption of water as the solution becomes more dilute. The other slight deviations from Beer's law are not greater than could be accounted for by the corrections mentioned under the discussion of the chloride curves.

Neodymium Acetate

Table IV gives the results obtained for solutions of neodymium acetate in water. The concentrations, reading from

Table IV—Transmissions of Neodymium Acetate Solutions

λ	D. = 2.5 mm. C. = 0.617 N	D. = 5 mm. C. = 0.308 N	D. = 10 mm. C. = 0.154 N	D. = 20 mm. C. = 0.077 N
686	98	97	94	94
693	92	91	93	95
698	97	97	96	93
704	98	100	92	93
708	96	98	92	96
712	100	96	94	96
716	100	94	90	94
720	94	90	90	94
723	87	87	79	76
726	69	64	60	57
730	44	36	32	30
733	22	22	18	21
737	24	17	14	15
741	30	23	22	25
746	41	39	34	35
751	52	55	52	55
755	71	71	65	67

759	81	84	81	82
763	90	91	87	88
767	93	93	89	87
770	94	90	87	89
774	89	88	83	84
779	72	74	74	75
783	62	63	59	55
787	45	40	37	32
791	24	21	17	18
796	22	17	17	14
800	27	28	27	28
805	57	46	44	46
809	69	63	62	64
814	74	76	73	75
819	90	83	83	82
825	92	89	86	87
830	92	93	92	91
834	98	98	92	91
839	96	97	94	90
845	97	97	90	88
850	95	96	90	87
856	95	94	84	83
861	91	83	77	71
867	72	69	65	67
872	62	60	56	53
877	66	67	58	57
882	71	72	66	66
888	83	82	76	75
894	87	84	81	78
900	91	88	84	79
906	92	90	87	83
912	94	90	90	82
917	96	93	89	85
923	97	96	94	86
933	99	95	91	83
938	99	95	92	77

left to right, were 0.617, 0.308, 0.154 and 0.077 normal, respectively, the corresponding depths of absorbing layer being 2.5, 5, 10 and 20 mm., respectively. The results in this table are plotted in Figs. XIII to XVI, inclusive. The percentage transmission and wave lengths are represented, respectively, by the ordinates and abscissas of the curves.

The minima of transmission fall at approximately the same

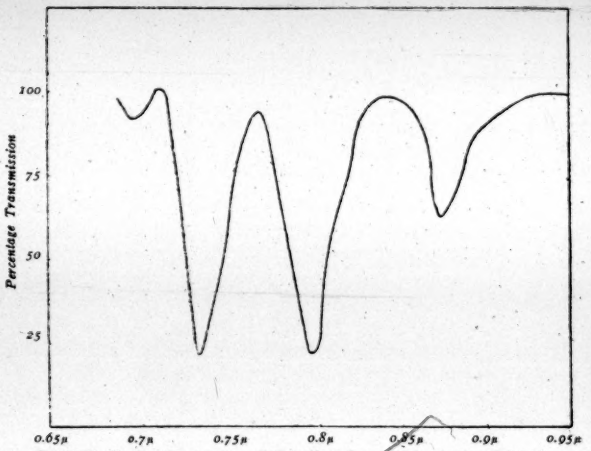

Fig. XIII—Neodymium Acetate. Cell depth, 2.5 mm.; concentration, 0.617 N

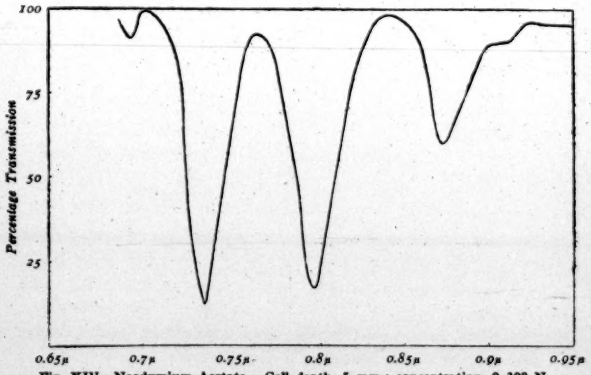

Fig. XIV—Neodymium Acetate. Cell depth, 5 mm.; concentration, 0.308 N

positions as with the chloride and nitrate solutions discussed above, i. e., at λ7300, λ7950 and λ8750. As indicated by the

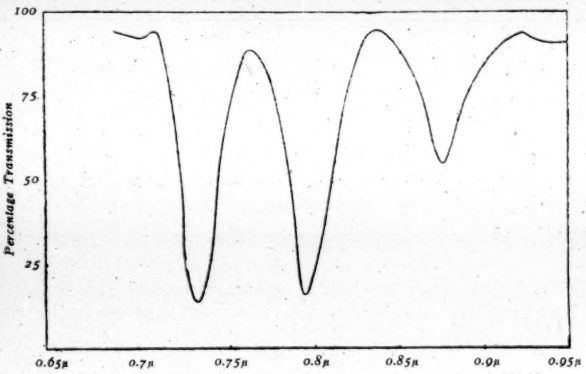

Fig. XV—Neodymium Acetate. Cell depth, 10 mm.; concentration, 0.154 N

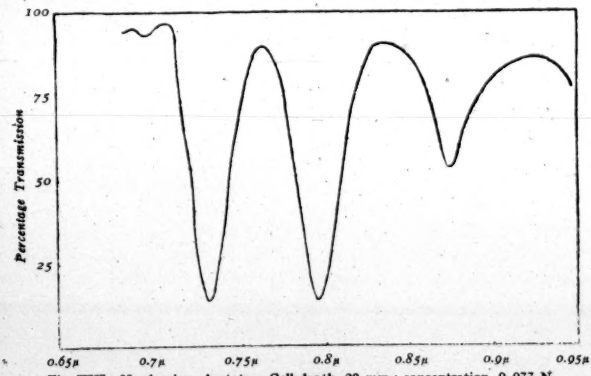

Fig. XVI—Neodymium Acetate. Cell depth, 20 mm.; concentration, 0.077 N

photographic method, the solutions of neodymium acetate have greater absorbing powers for a given concentration than either the chloride or nitrate.

The small band near λ7000 appears slightly more intense with the acetate than with equal concentrations of the other salts; and the more intense bands λ7300, λ7950 and λ8750 show the same general tendency to have their minima lowered with increasing dilution. This set of curves shows in a marked way the rapid increase in the absorption near λ9500, which is due to the water present in the solution, and illustrates the difficulty that is met with when working with aqueous solutions at greater wave lengths than 1μ. Even over the range of wave lengths at which we have worked, it is seen that the absorption due to water is a disturbing factor.

Praseodymium Chloride

Solutions of praseodymium salts are not of great interest, from our standpoint, in those regions beyond the visible part of the spectrum. It was found that such solutions were transparent in the infrared end of the spectrum as far as 1.5, except two very weak bands which fall just in the midst of the intense water bands. Since, at this point, a very thin layer of water is almost completely opaque, it is evident that it would be impossible to study aqueous solutions in this region, especially dilute solutions.

As shown by the photographic plate, praseodymium salts possess two groups of bands in the visible spectrum, one in the green near λ4600 and another near λ5900. Since the amount of energy at the former wave length is so very small, the width of slits necessary to be used was too large to give satisfactory results. Such bands could, of course, be detected, but the deflections of the instrument at this part of the spectrum are very small, and, hence, relatively large errors would occur in making the readings.

For this reason we have confined our attention to a careful study of the one band which has its center near λ5900. Table V gives the observed transmissions for the four dilutions of solutions of praseodymium chloride. In column 1 there is given λ taken at such intervals as the graduated head of the spectroscope would permit. Reading from left to right, the respective concentrations were 1.377, 0.688, 0.344 and 0.177

normal, the corresponding depths of absorbing layer being 2.5, 5, 10 and 20 mm., respectively.

PROPERTY OF CASE LIBRARY

Table V—Percentage Transmissions of Praseodymium Chloride Solutions

λ	D. = 2.5 mm. C. = 1.377 N	D. = 5 mm. C. = 0.688 N	D. = 10 mm. C. = 0.344 N	D. = 20 mm. C. = 0.177 N
506	100	100	100	100
518	100	98	100	100
530	100	98	100	100
544	99	99	99	98
556	99	99	99	98
563	100	98	100	98
565	99	99	98	97
567	97	100	98	97
572	97	99	95	97
577	96	98	93	95
579	91	92	90	92
583	85	86	84	80
585	77	76	70	72
587	60	59	55	56
589	45	46	40	40
592	35	35	32	33
595	35	34	34	33
597	43	43	42	42
600	56	56	56	56
602	69	69	68	69
605	81	82	81	81
607	90	92	88	88
611	93	94	93	94
614	97	99	95	97
629	98	100	97	98

In terms of Beer's law, the curves representing these tables should be identical. Such curves are represented by Fig. XVII. Beginning with the curve nearest the left and proceeding towards the right, the succeeding curves represent the four dilutions of praseodymium chloride as given in the preceding paragraph.

The curve representing the most concentrated solution is nearest the left of the figure. It is seen that these curves are identical to within the limits of experimental error; the slight increase in the absorption with dilution is to be attributed to

the slit width correction. The slit width was in every case 0.4 mm. Water has no absorption in this region.

The results recorded in these curves are in agreement with previous photographic results. The minimum in transmission, which in each case is about 30 per cent., occurs near λ5900. The total deviation from Beer's law over the dilution studied

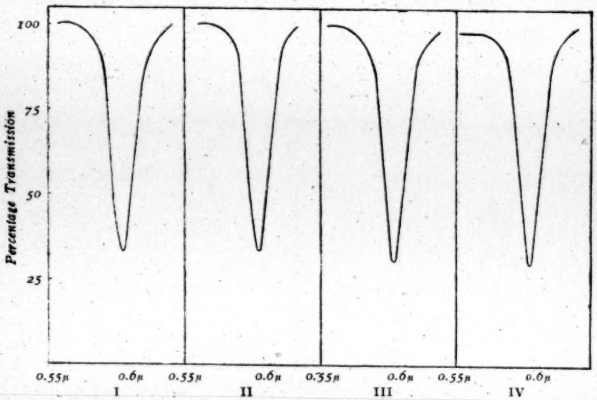

Fig. XVII—Praseodymium Chloride. I. Cell depth, 2.5 mm.; concentration, 1.377 N. II. Cell depth, 5 mm.; concentration, 0.688 N. III. Cell depth, 10 mm.; concentration, 0.344 N. IV. Cell depth, 20 mm.; concentration, 0.177 N.

is not over 3 per cent., which is well within the experimental error in this portion of the spectrum.

Praseodymium Nitrate

Corresponding results for solutions of praseodymium nitrate are given in Table VI. The concentrations of the solutions, beginning on the left and reading towards the right, were 1.282, 0.641, 0.320 and 0.161 normal, respectively, the corresponding depths of absorbing layer being 2.5, 5, 10 and 20 mm., respectively.

Table VI—Percentage Transmissions of Praseodymium Nitrate Solutions

λ	D. = 2.5 mm. C. = 1.282 N	D. = 5 mm. C. = 0.641 N	D. = 10 mm. C. = 0.320 N	D. = 20 mm. C. = 0.160 N
506	100	100	99	100
518	98	98	100	100
530	100	100	99	99
544	99	98	100	100
556	99	98	100	98
563	99	99	98	97
565	96	100	98	96
567	98	100	98	97
572	90	97	96	95
577	93	92	94	93
579	90	92	90	91
583	83	86	85	83
585	73	74	72	72
587	62	60	60	58
589	48	46	46	45
592	40	40	38	36
595	37	36	36	36
597	44	44	44	42
600	56	56	56	54
602	68	67	68	67
605	79	82	79	80
607	87	89	89	88
611	91	92	94	92
614	95	95	97	96
629	98	98	99	98

The results are plotted in Fig. XVIII. Reading from left to right, there is shown the effect of increased dilution on solutions of praseodymium nitrate, and such concentrations and depths of absorbing layers as were mentioned above, the most concentrated solution being nearest the left of the figure.

As with the curves representing the solutions of praseodymium chloride, these curves show that Beer's law holds quantitatively for solutions of the nitrate. Neither the position nor the intensity of the band is altered more than the limits of error of our work for the range of dilution studied. It may be recalled that this is in exact agreement with the photographic results recorded elsewhere in Monograph 190 of the Carnegie Institution.

Salts of Nickel

Table VII gives the percentage transmission of the nickel salts studied. Beginning at the left of the table, column 1 gives λ, taken at such intervals as the solutions required, and reading towards the right are the results for the following

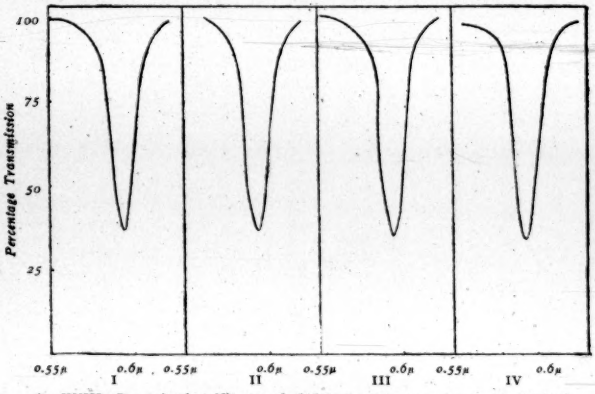

Fig. XVIII—Praseodymium Nitrate. I. Cell depth, 2.5 mm.; concentration, 1.282 N. II. Cell depth, 5 mm.; concentration, 0.641 N. III. Cell depth, 10 mm.; concentration, 0.320 N. IV. Cell depth, 20 mm.; concentration, 0.160 N.

salts: Nickel chloride, depth of cell 3 mm.; concentration, 2.74 normal; nickel nitrate, depth of cell 5 mm.; concentration 1.68 normal; nickel sulphate, depth of cell 5 mm.; concentration 1.108 normal, respectively.

Curves representing these results are given in Figs. XIX, XX and XXI.

Table VII—Percentage Transmissions of Solutions of Nickel Salts

λ	Nickel chloride D. = 3 mm. C. = 2.74 N	Nickel nitrate D. = 5 mm. C. = 1.68 N	Nickel sulphate D. = 5 mm. C. = 1.108 N
544	71	69	81
556	64	69	79
563	62	65	76
565	60	61	73
577	56	57	68

583	52	50	66
587	47	46	61
592	40	40	60
597	34	33	40
602	26	28	43
607	22	22	37
614	17	17	33
618	12	12	26
625	10	9	23
632	8	6	18
638	5	6	15
643	3	4	12
650	0	4	12
662	0	3	10
676	0	2	10
693	0	9	11
755	7	8	10
770	7	8	18
779	11	13	20
787	14	17	30
796	16	20	33
805	18	24	40
814	22	31	44
825	28	36	49
834	32	40	55
845	36	46	58
856	41	48	64
867	46	51	66
877	49	52	68
888	51	56	69
900	53	56	68
912	54	56	67
923	52	51	64
933	50	48	62
938	47	44	59
955	42	38	52
966	36	30	44
978	30	24	38
990	26	20	33
1002	22	16	28
1012	20	14	24
1023	15	9	22
1035	13	8	20
1047	9	4	17
1060	6	4	14

Nickel Chloride

Fig. XIX, the curve for nickel chloride, shows an increasing absorption from 70 per cent. transmission at λ5200 to complete absorption at λ6300. From this point there is complete absorption to the regions λ7200, and then a gradual increase in transmission, reaching a maximum of 53 per cent. near λ9000, then decreasing again to zero transmission at λ10000.

As has been shown photographically, the visible spectrum of salts of nickel consists of intense broad absorption bands both in the blue and red, showing a single region of transmission extending to about λ6500 in the red. It is interesting to note that by means of the radiomicrometer we are able to study another region of transmission which reaches a maximum near λ9000. From this point the absorption rapidly increases until the region of water absorption is reached. It was not possible to determine whether the solution again became transparent beyond this point, on account of the water absorption.

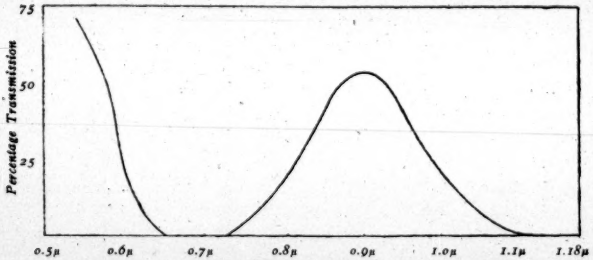

Fig. XIX—Nickel Chloride. Cell depth, 3 mm.; concentration, 2.74 N

Nickel Nitrate

Fig. XX, which represents the second column of Table VII, gives the transmission, as observed, for a solution of nickel nitrate, concentration 1.68 normal and 5 mm. absorbing layer. This figure is almost exactly analogous to the curve for nickel chloride, just discussed in the preceding paragraph, and shows maxima at λ5400 and λ9000. There is complete absorption in the region λ7000 and beyond 1.1μ. Figs. XIX and XX

represent approximately equal amounts of the chloride and nitrate, respectively, and are very similar.

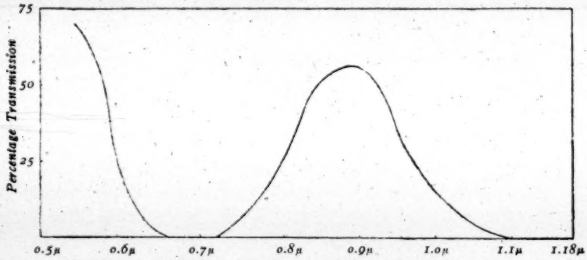

Fig. XX—Nickel Nitrate. Cell depth, 5 mm.; concentration, 1.68 N

Nickel Sulphate

The curve representing the last column of this table is given in Fig. XXI. The concentration of nickel sulphate was 1.108 normal, and the depth of absorbing layer was 5 mm.

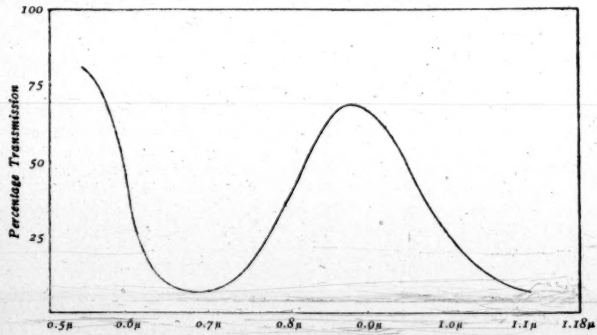

Fig. XXI—Nickel Sulphate. Cell depth, 5 mm.; concentration, 1.108 N

It will be seen that this solution is slightly more dilute than the other two solutions of nickel salts studied, and that in no region does the curve representing the transmission reach complete absorption. Maxima in transmission appear near λ5400

and λ9000 and minima of about 8 per cent. at λ6900 and λ11000. Readings were not made at greater wave lengths with any of the nickel salts, on account of the intense water absorption slightly beyond this region.

No striking or characteristic difference is noted in the absorption as shown by the three curves representing the three salts of nickel studied. Each of them shows maxima and minima in about the same region of the spectrum.

Salts of Cobalt

The photographic plate shows that in the visible region salts of cobalt have a strong ultraviolet absorption, a band in the orange near λ5000, and increasing transmission from the center of this band toward the longer wave lengths. It was interesting to see whether solutions of cobalt salts were completely transparent beyond the limit of sensibility of the photographic plate, or if such solutions again showed absorption bands in the infrared. It was also of interest to know whether equal concentrations of the different salts showed the same or different absorption bands. With this idea in view, the solutions of five salts of cobalt were studied. In each case the concentration was 0.347 normal, and the depth of absorbing layer 10 mm.

The results are given in Table VIII. Beginning at the left are given, in their respective order, the observed transmissions

Table VIII—Transmissions of Cobalt Solutions

λ	Cobalt chloride 10 mm. = 0.347 N D. C.	Cobalt bromide 10 mm. = 0.347 N D. C.	Cobalt nitrate 10 mm. = 0.347 N D. C.	Cobalt sulphate 10 mm. = 0.347 N D. C.	Cobalt acetate 10 mm. = 0.347 N D. C.
544	12	21	20	14	15
556	19	33	31	26	31
572	39	50	35	48	53
583	48	61	64	57	59
589	59	68	68	62	69
592	63	74	73	67	72
605	68	74	77	67	72
614	70	74	77	68	74
622	72	74	79	68	75

632	72	75	84	69	76
640	72	75	76	70	77
650	73	76	79	71	76
660	73	78	81	72	80
667	74	78	82	74	83
678	79	82	85	77	84
686	80	84	88	79	85
693	81	85	90	88	88
708	84	87	91	81	89
720	84	89	91	82	92
730	85	87	92	83	89
741	88	88	88	82	91
755	87	89	89	83	91
767	87	92	89	82	92
779	88	89	89	84	90
791	90	89	89	83	90
805	91	89	87	84	89
819	88	88	84	83	90
834	87	87	83	83	86
850	88	86	76	80	86
867	88	95	95	80	85
882	84	84	82	79	83
900	84	81	77	76	84
917	83	82	79	77	82
933	78	77	79	73	78
949	70	69	70	66	70
966	58	55	56	54	56
984	51	49	50	47	52
1,002	49	48	50	47	49
1,018	51	50	50	47	52
1,035	51	50	53	50	52
1,053	48	50	56	49	52
1,072	46	46	50	44	48
1,091	41	41	46	40	41
1,109	34	35	39	34	36
1,123	29	31	35	30	32
1,136	24	25	23	24	25
1,147	17	21	14	16	19
1,162	12	12	13	11	12
1,174	9	10	11	10	10
1,187	9	9	10	9	9
1,202	8	8	9	8	10

for 10 mm. of solution of the following salts: Cobalt chloride, cobalt bromide, cobalt nitrate, cobalt sulphate and cobalt acetate.

The results of Table VIII are plotted as transmission curves in Figs. XXII to XXVI, inclusive. A study of these curves shows that they are very similar, all having maxima of trans-

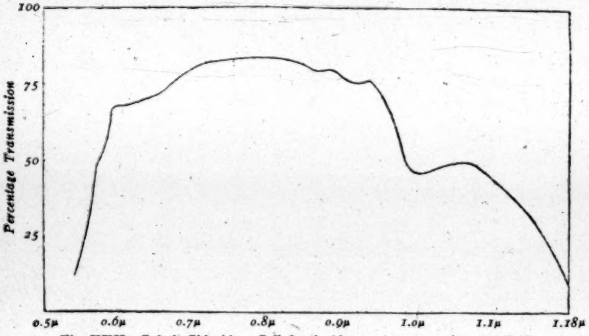

Fig. XXII—Cobalt Chloride. Cell depth, 10 mm.; concentration, 0.347 N

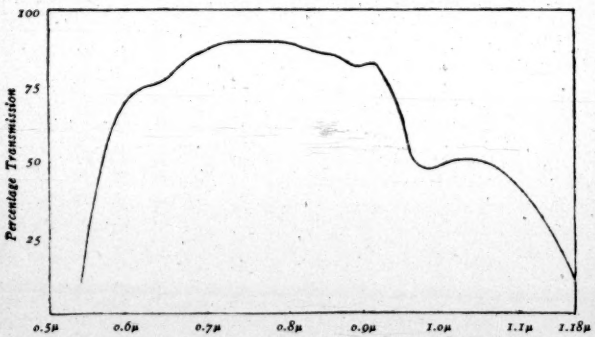

Fig. XXIII—Cobalt Bromide. Cell depth, 10 mm.; concentration, 0.347 N

mission at the following points: λ5950, λ7800, λ9100 and λ10,600. In general, for all the salts of cobalt studied, the transmission curves rise rapidly from λ5000 to λ5900, where the transmission reaches about 65 per cent. The curves show

a broad but slight absorption over the region near λ6500, and reach a maximum transmission over the region near λ7000 to λ8000. The curves then descend, showing a series

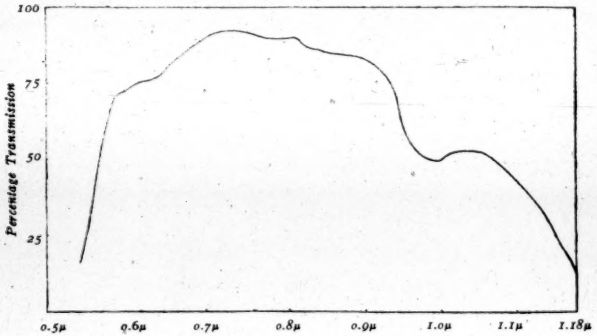

Fig. XXIV—Cobalt Nitrate. Cell depth, 10 mm.; concentration, 0.347 N

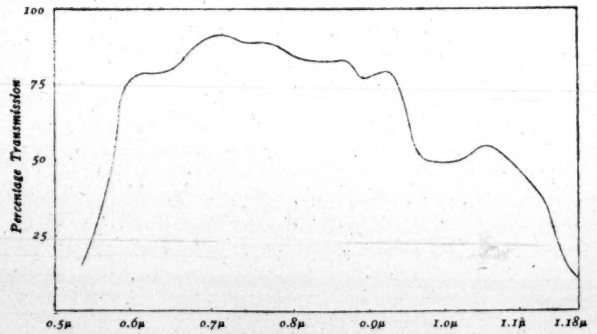

Fig. XXV—Cobalt Sulphate. Cell depth, 10 mm.; concentration, 0.347 N

of small absorption regions near λ8400, λ8900 and λ9800. The last of these absorption bands shows a fairly sharp edge towards the shorter wave lengths. Beyond λ10,500 the absorption

increases rapidly until the region is reached where water is practically opaque.

Fig. XXV, representing the curve of transmission of cobalt

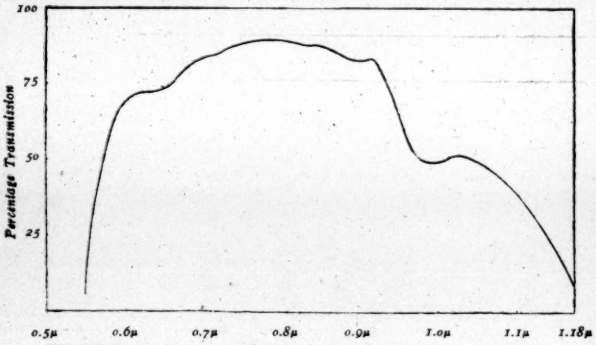

Fig. XXVI—Cobalt Acetate. Cell depth, 10 mm.; concentration, 0.347 N

sulphate, appears slightly different from the curves of the other salts of cobalt, having better defined bands in the region of λ8000.

GENERAL DISCUSSION OF THE RESULTS OBTAINED WITH THE RADIOMICROMETER

The introduction of the *radiomicrometer* into the work converted it into a quantitative study of the absorption spectra of solutions. The grating spectroscope and photographic method were very efficient in locating the positions of the absorption lines and bands from wave lengths λ2000 to about λ7600; and the photographic method gave some approximate idea as to the intensities of the various lines and bands. This method is, however, only roughly quantitative, and is very limited in the range of wave lengths to which it can be applied.

The radiomicrometer provides us with a quantitative method for studying the intensities of the various lines and bands, and also greatly extends the range of wave lengths that can be studied. In the earlier work with the radiomicrometer much time and labor were expended in perfecting the instrument,

especially in constructing a sensitive radiomicrometer with a short period. Dr. Guy accomplished this very successfully.

The earlier work was practically limited to the study of the absorption spectra of solutions of neodymium salts—neodymium chloride, bromide, nitrate and acetate.

The results were plotted in what is known as transmission curves, which express the percentage transmission for the different wave lengths. Solutions of different concentrations of a given salt were studied, the depth of layer of the solution varying inversely as its concentration. The product of the depth of layer times the concentration is a constant. If the solvent plays no role in the absorption, then the transmission curves for the different concentrations of any given salts must fall directly over one another—the different curves would be the same curve.

We found that, in general, the more concentrated the solution the less the transparency and the broader the absorption bands; this is exactly what we obtained with the grating spectroscope and the photographic method. But in the more dilute solution the intensity of the bands was greater. We observed further that with increase in dilution the middle of the band is displaced towards the longer wave lengths.

The same general changes with dilution in the absorption spectra of solutions of neodymium bromide were observed as with the chloride; the more dilute the solution the narrower and more intense the bands.

The bands of neodymium nitrate, in general, show the same changes with dilution as those of the chloride and bromide. With increase in dilution the intensities of the bands increase, and their centers are displaced somewhat towards the longer wave lengths.

The three salts of neodymium, then, all show an increase in intensity with dilution. A possible explanation of this phenomenon, based upon resonance, has been offered. It is a well-known fact that a resonator, when excited by vibrations from a single vibrating resonator having the same pitch, vibrates more strongly than when set into vibration by a large number of resonators, one of which has the same pitch as its

own and the others slightly different periods. In a word, if several vibrators are near together, every one exerts a certain influence on the others. The result is that no one of them has exactly the same period as the original resonator. Each resonator damps the other and we have less perfect resonance.

In a concentrated solution the resonators are relatively close together and mutually affect one another. The result is imperfect resonance, and the absorption bands are less intense in the more concentrated solution.

In the more dilute solution the vibrators are farther removed from one another and are surrounded by large amounts of water of hydration. The damping effect would thus be diminished. In such cases we would have more perfect resonance and the resulting absorption bands would be more intense.

Subsequent work has, however, shown that a part of this effect can possibly be explained as due to the fact that the slit width used was not infinitesimal.

It was found by the radiomicrometer, as with the grating spectroscope and photographic plate, that for a given concentration the acetate absorbs much more than any other salt of neodymium.

One of the most interesting facts thus far established by means of the radiomicrometer is the *effect of the dissolved substance on the absorption spectra of water*. We noted that aqueous solutions of hydrated salts were often more transparent than pure water. This is obviously a very remarkable fact, and we at once took up its careful study. We compared the absorption of aqueous solutions of strongly hydrated salts with the absorption of a layer of water equal in depth to the water in the solution through which the light was passed. We then carried out similar experiments with salts which, in the presence of water, combine with only a small amount of it. In a word, we compared the absorption of light by water with the absorption of an equal depth of water in aqueous solutions of strongly hydrated salts, and the absorption of light by water with an equal depth of water in aqueous solutions of salts which are scarcely hydrated at all.

The nonhydrated salts with which we worked were potassium chloride, ammonium chloride, and ammonium nitrate. It was necessary in all of this work to choose salts which themselves have little or no absorption in the region in which water absorbs, i. e., in the infrared. It was found that aqueous solutions of the above-mentioned compounds showed the same absorption of light as water having the same depth as the water in the solutions in question. This is exactly what would be expected. The dissolved substance and the solvent do not combine with one another to any appreciable extent, and it would be very difficult to see how either could appreciably affect the absorbing power of the other.

When we turn to the strongly hydrating salts, very different relations manifest themselves. The salts of this class that were studied were calcium chloride, magnesium chloride and aluminium sulphate.

In the case of a 5.3 normal solution of calcium chloride, the solution is the more transparent from 0.9μ nearly to 1μ. The water then becomes the more transparent for a short distance. From 1.05μ to 1.2μ the solution is the more transparent, becoming as much as 25 per cent. more transparent than the pure water. The water becomes more transparent than the solution only at and near the *bottom of the "water bands"* at approximately 1μ. This is what we should expect if the solute exerts a damping effect on the absorbing power of water. When a smaller depth of the solution of calcium chloride is used, the water in the region 1.25μ is more transparent than the solution. From this band on to the longer wave lengths the solution becomes more transparent than the water until 1.42μ is reached, when both solution and water are practically opaque.

The results for magnesium chloride are essentially the same as those obtained for calcium chloride. The main difference is that from 1.0μ to 1.1μ, in the case of magnesium chloride, the water is more transparent; while for calcium chloride in this region the solution is the more transparent. The difference between water and the solution of magnesium chloride in this region is, however, not great. For longer wave lengths than 1.1μ, the solution of magnesium chloride, like the solu-

tion of calcium chloride, is more transparent than the water, the difference for the two salts being of the same order of magnitude.

When a smaller depth of layer of the solution was used, the water was the more transparent from 1.22μ to 1.34μ. For the longer wave lengths the solution was the more transparent.

The curve for aluminium sulphate brings out this new feature: at 1μ the solution is more transparent than the water. Beyond 1.04μ the water is transparent to 1.17μ, beyond which the solution is the more transparent, as with magnesium and calcium chlorides.

In the region of 1.2μ water is the more opaque when a shallower layer of solution is used. From 1.29μ to 1.36μ, water is the more transparent; beyond 1.36μ the solution is the more transparent.

The explanation of these remarkable results is that they must be due to some action of the dissolved substance on the solvent. That the solvent can affect the absorption spectra of the solution was first shown by Jones and Anderson;[1] and a large number of examples of this same action has since been found by Jones and Strong.[2] The action was satisfactorily explained as due to a combination of the solvent with the dissolved substance, and this explanation accounted for many facts which could not be otherwise satisfactorily explained. This theory of solvation in solution has aided us in explaining many phenomena which the theory of electrolytic dissociation alone could not account for, as has frequently been pointed out.

The same solvate theory of solution seems to aid us in explaining the facts just discussed. Those substances that do not form hydrates when in the presence of water show normal results as far as absorption spectra are concerned. Their solutions have the same absorption as so much pure water, the substance itself showing no absorption.

It is the hydrated salts, and only these, which give the abnormal results herein recorded. *The combined water seems to have less power to absorb light than free or uncombined water.* This would account for all of the facts observed.

[1] Carnegie Institution, Washington, Publication 110.
[2] *Ibid.*, 130 and 160.

It should be noted that the presence of the salt shifts the absorption of the water towards the longer wave lengths. It was earlier observed that rise in temperature and increase in concentration shifted the absorption of the salt towards the longer wave lengths. The effect of rise in temperature and of increase in concentration is to simplify the hydrates existing in the solution. This simplified resonator shifts the absorption towards the red. The effect of the salt on the absorption of the water is the same as rise in temperature and increase in the concentration of the solution on the absorption of the dissolved substance. It may be that the dissolved substance diminishes the association of the solvent and thus simplifies the resonator. This may be true especially with the water of hydration or the water combined with the dissolved substance.

This new line of spectroscopic evidence bearing on the solvate theory of solution is regarded as probably the most direct that we have or can hope to obtain in favor of the view that there is combination between solvent and solute.

In studying the *absorption spectra of salts*, the intensity of the light after passing through the solution of the salt in question was compared with the intensity of the light after passing through a depth of water equal to the water in the solution in question.

The absorption spectrum of neodymium chloride shows three pronounced minima representing the three absorption bands with their centers near $\lambda 7300$, $\lambda 7950$ and $\lambda 8700$, and less pronounced bands near $\lambda 7150$ and $\lambda 9000$. The latter may be due in part to the solvent; for all four dilutions studied the $\lambda 7300$ and $\lambda 7900$ bands show complete absorption over a considerable range of wave lengths. The minimum of band $\lambda 8700$ is gradually lowered with increasing dilution.

The maximum transmission of solutions of neodymium chloride occur near $\lambda 7600$ and $\lambda 8400$, these solutions becoming almost completely transparent beyond 1μ, except for the absorption of the solvent of this region. It seems that Beer's law holds, in general, for the infrared absorption of solutions of neodymium chloride.

The minima in the curves for the more dilute solutions of neodymium chloride are in about the same positions as those in the more concentrated solutions, but the solutions being more dilute are more transparent; hence the minima are not so pronounced. The maximal absorption occurs near λ7300 and λ7900. The λ8700 band has a minimum transmission of 64 per cent. There is complete transmission in the regions λ7200, λ7600, λ8300 and λ9300. The drop in all of the curves beyond 0.9μ is due to the absorption of the water.

With further increase in the dilution of the solution, there is a lowering of the maxima. The change is most pronounced in the λ8700 band, and here the absorption of the water is the most pronounced. The absorption of the water, together with the correction for its width, may account for this change, and Beer's law may hold for the dilute solutions of neodymium chloride almost as well as for the more concentrated.

Neodymium nitrate shows three minima at λ7300, λ7950 and λ8750. The nitrate bands are not as intense as those of the chloride, the solution of the nitrate not being as concentrated as that of the chloride. The nitrate bands, like those of the chloride, become more intense with increase in dilution. The absorption of water becomes more and more pronounced beyond 1μ.

The minima for solutions of neodymium acetate fall at approximately the same positions as with the chloride and nitrate.

Solutions of neodymium acetate, as indicated by the photographic method, show greater absorbing power than those of either the chloride or nitrate. The λ7000 band is slightly more intense in the acetate. The more intense bands, λ7300 and λ7950, show the same tendency to have their minima lowered with increasing dilution. There is a rapid increase in the absorption near λ9500, due to the water present in the solution.

Solutions of praseodymium salts are transparent in the infrared as far as 1.5μ, except two very weak bands which fall in the midst of the intense water bands. Praseodymium salts have two groups of bands, one in the green near λ4600 and

another near λ5900. We have limited our investigations to the latter band, on account of the small amount of energy transmitted at λ4600. The curves representing the absorption of different concentrations of praseodymium chloride are identical to within the limits of possible experimental error. The results obtained with the radiomicrometer are in accord with those found by the grating and photographic plate. The minimum in each case occurs near λ5900. The total deviation from Beer's law, as shown by solutions of praseodymium chloride, is within the limits of experimental error.

The curves for praseodymium nitrate show that Beer's law holds here as well as for the chloride.

Solutions of nickel chloride show an increasing absorption from λ5200 to λ6300, where it is complete. Complete absorption extends to λ7200. Transmission increases to λ9000, then decreases to zero at λ10000. The visible spectrum of salts of nickel consists of intense broad absorption bands in the blue and red, having a single region of transmission in the red, extending to about λ6500. By means of the radiomicrometer we could study the region of transmission near λ9000. Beyond this we could not go because of the absorption of water.

The absorption of nickel nitrate closely resembles that of the chloride. There is maximal absorption at λ5400 and λ9000. There is complete absorption in the region λ7000 and beyond 1.1 μ.

The solution of nickel sulphate studied is slightly more dilute than the chloride and nitrate. In no region is there complete absorption. There is maximal transmission near λ5400 and λ9000, and minima at λ6900 and λ11000. Readings were not extended beyond this region on account of the intense absorption of water. The three salts of nickel studied have just about the same absorption spectra, the curves showing maxima and minima in just about the same regions of the spectrum.

Salts of cobalt in the visible region have a strong ultraviolet absorption. There is a band in the orange near λ5000, and increasing transmission towards the red. The infrared absorption of solutions of cobalt salts was studied, and the ab-

sorption of the chloride, bromide, nitrate, sulphate and acetate compared. The transmission curves for all of these salts have maxima at λ5950, λ7800, λ9100 and λ10600.

The transmission curves for all of the salts of cobalt studied rise rapidly from λ5000 to λ5900. The curves show a broad, slight absorption over the region near λ6500, and reach a maximum transmission from λ7000 to λ8000. There is a series of small absorption regions near λ8400, λ8900 and λ9800. Beyond λ10500 the absorption increases rapidly to the region where water is practically opaque.

The curves for cobalt sulphate are slightly better defined than those of the other cobalt salts.

In conclusion, we wish to express our thanks to Prof. A. H. Pfund for valuable suggestions, and to Dr. E. J. Shaeffer, who assisted in making the readings.

JOHNS HOPKINS UNIV.
1913

DOUBLE CHLORIDES OF FERRIC AND FERROUS IRON WITH SOME AROMATIC BASES[1]

BY RAPHAEL MONROE MCKENZIE

Up to the time of beginning this work no double halides of iron and organic bases had been prepared and only a few such compounds containing metallic halides. In 1894 Walden[2] published the results of a systematic study of the double halides of ferric iron with rubidium, caesium, potassium and ammonium and found that they all conformed to Remsen's law,[3] as did all such compounds that had previously been described. In this investigation the double chlorides of ferric iron with aniline, *o*-, *m*- and *p*-toluidine, and of ferrous iron with aniline and with *o*-toluidine are described.

[1] Abstract of a dissertation submitted to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The work was completed a number of years ago and the results would have been published sooner but for the fact that it seemed desirable to repeat a part of it. This has been prevented and it seems best now to publish the results without further delay. The investigation is one of a series undertaken with the object of testing a generalization arrived at regarding the composition of the double halides (THIS JOURNAL, **11**, 291).—I. R.

[2] Am. J. Sci., [3] **48**, 283.

[3] THIS JOURNAL, **11**, 291.

Methods of Analysis

Purification.—To purify the salts for analysis they were filtered off with the aid of the pump, pressed between layers of filter paper to dryness, and the last of the hydrochloric acid extracted by letting them stand in a desiccator over sulphuric acid and solid potassium hydroxide. This method, slightly modified, was used by Neumann.[1] The analytical results were often not as close to the values required by the theory as could be desired, owing to the method of formation and of purification, and to the properties of the salts. They are all decomposed by water and can be recrystallized only from concentrated hydrochloric acid. Some of them are decomposed even by the concentrated acid, the hydrochlorides of the organic base separating alone from the solution on cooling.

Iron.—The weighed salt was dropped into a porcelain dish containing an excess of a weak solution of potassium hydroxide. The dish was then heated on a sand bath until the solution no longer gave any odor of aniline or of toluidine, water being added from time to time. An excess of hydrochloric acid was then added. As in many cases the organic base had caused some reduction, a small amount of hydrogen peroxide was added, and the solution was then evaporated to dryness. A little more acid was now added, and it was again evaporated to dryness. In the case of ferrous salts the oxidation with hydrogen peroxide was, of course, always required. The ferric chloride was then filtered into a pressure bottle through washed asbestos, to separate any precipitate formed by action on the aniline. The filtrate was then treated with a solution of potassium hydroxide until a slight permanent precipitate of ferric hydroxide separated; 0.2 cc. of dilute hydrochloric acid was added, and 1 gram of potassium iodide introduced. The bottle was then closed and heated at about 60° for twenty minutes. After cooling, the iodide set free was titrated in the bottle by use of starch and a solution of sodium thiosulphate, 1 cc. of which corresponds to 1 milligram of iron. The results were quite satisfactory.

[1] Ann. Chem. (Liebig), **244**, 33.

The use of an open dish in place of a flask when boiling off the aniline or toluidine greatly lessened the time required. The use of the open dish and the evaporation of the ferric chloride to dryness were found necessary to ensure the complete removal of the hydrogen peroxide. The hydrogen peroxide is more stable than was formerly supposed.[1] It was found that hydrogen peroxide passed off with the steam and condensed on the side of a flask running back into the solution and causing error in analysis. The water which condensed on a watch glass held in the steam above the flask also gave a strong reaction for hydrogen peroxide when tested with iodized starch paper.

Chlorine.—A weighed sample of the salt was dropped into an Erlenmeyer flask containing a solution of pure potassium hydroxide, which was in excess of the amount required to decompose the salt. The alkaline solution was then boiled until the odor of aniline or toluidine was no longer noticed in the steam given off. Then the solution, formed on dissolving the ferric hydroxide in an excess of nitric acid, remained colorless. If all the organic base had not been driven off with the water vapor, a colored solution was formed. To the acid solution 5 cc. of a saturated solution of ferric ammonium alum was added, and the cold solution was titrated by Volhard's method in the flask.

In the case of the ferrous salts, a cold solution of the salt in very dilute nitric acid could be titrated directly without boiling off the organic base. But in most cases the method given above was used.

Water of Crystallization.—All attempts to make quantitative determinations of the water in these salts were unsuccessful. Samples of the salts, placed in the sulphuric acid desiccator, did not come to constant weights even after standing more than a month. It was found that the inside of the desiccator and the watch glass containing the salt became coated with a sublimate.

Samples of the salts were heated at 90°–110° in a glass tube, the closed end of which was placed in an air bath while

[1] Ber. d. chem.Ges., **27**, 3307.

the other end extended out into the air. Here it was found that a sublimate was deposited on the cool part of the tube. These trials showed that the water could not be determined by difference.

It was then thought that the water might be determined by absorption in a drying tube. To try this a sample of the salt was heated in a porcelain boat, within a glass tube which extended through an air bath. Air was drawn slowly through the tube while the air bath was heated to 100°, when it was found that the aniline hydrochloride and also the toluidine hydrochloride sublimed and were deposited on the cooler parts of the tube, while the water was carried farther to still colder portions of the tube. To determine whether water alone was carried on by the air current, a U-tube, containing a solution of silver nitrate, was attached to the front end of the tube and the air was drawn through it. After a few minutes the solution became cloudy and a precipitate formed, showing that compounds containing chlorine were carried over. This prevented further attempts being made to determine the water quantitatively.

The presence or absence of water was determined qualitatively, thus: The combustion tube was united to a drying tube, at the back, and to an empty, dry U-tube, and this to a drying tube, at the front. The U-tube was cooled by placing it in cold water. The salt was heated in the porcelain boat as before, and air was drawn through the system. If the salts contained water it was deposited on the walls of the U-tube as dew or in drops, the amount deposited giving some idea of the proportion of water in the salt and confirming the analytical results.

Some of the salts were analyzed before this method was used and in these cases nothing has been said as to the water, though the analytical results require the assumption that water was contained in them.

The atomic weights used in the calculations were: H, 1; O, 16; N, 14; Cl, 35.4; Fe, 56; C, 12.

Oxidation of Ferric Chloride

Much difficulty was experienced in the early part of the work,

owing to the tendency of ferric chloride to oxidize the organic base. Thus, when a solution of ferric chloride and aniline hydrochloride was heated, the aniline was decomposed[1] and the ferric chloride reduced. In many cases a blue flocculent precipitate separated in such quantity as to fill the solution. In other cases it separated in smaller amounts, but interfered with obtaining pure salts. Slightly acid solutions were made in the ratio of one molecule of ferric chloride to two molecules of aniline hydrochloride, of one to four and of one to five. The first solution became light green on mixing and darkened on heating, when it became filled with the blue precipitate. The second solution with a smaller proportion of ferric chloride was lighter green than the first, but on heating and standing it darkened, and the precipitate formed. The third solution had a yellowish green color on mixing, but on heating, the upper layer, exposed to the air, became green; then the precipitate started to form and soon spread through the whole solution.

It was found later that the oxidizing action of the ferric chloride was greatest in slightly acid solution and that it was decreased by the addition of strong hydrochloric acid. Solutions made up by dissolving the aniline hydrochloride in a mixture of three parts concentrated hydrochloric acid to one part of water, and adding the ferric chloride, could be boiled with little or no formation of the precipitate.

In the work on *o*-toluidine hydrochloride it was found that the oxidizing action of the ferric chloride could not be prevented by increasing the amount of acid in the solution. Even solutions which had been saturated with hydrochloric acid gas decomposed on heating.

Ladenburg[2] describes the product formed by the action of ferric chloride on *o*-toluidine hydrochloride as the blue dye—toluidine blue—which separates as a flocculent precipitate. It is colored green by hydrochloric acid. The *p*-toluidine hydrochloride does not form such a compound. These results were confirmed in this work.

[1] Jegel: Jahresb. chem. Technologie, **1875**, 955.
[2] Ber. d. chem.Ges., **1877**, 1127.

This behavior of *o*-toluidine hydrochloride led to some qualitative experiments as to the relative ease and rate of oxidation of aniline hydrochloride, and of *o*-, *m*- and *p*-toluidine hydrochlorides by ferric chloride.

These experiments showed that *o*-toluidine hydrochloride is the most readily acted on by the ferric chloride; *m*-toluidine hydrochloride comes next; aniline hydrochloride is less easily attacked, while *p*-toluidine hydrochloride is not acted on, as will also be seen later.

Dianiline Chloroferrate,

$FeCl_3.2C_6H_5NH_3Cl$

Solutions of ferric chloride and aniline hydrochloride in the ratios of 2 molecules of the former to one of the latter, of 3 : 1, of 4 : 1, and of 8 : 1, give this salt. The 2 : 1 and 3 : 1 solutions may give, first, the hexaniline chloroferrate, and then—on further concentration—a crop of this salt.

Solution in the Ratio of 2: 1.—A solution was made by adding 16 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, about 50 cc. of hydrochloric acid, i. e., nearly three parts of the concentrated acid to one part of water, and dissolving in it 2.4 grams of aniline hydrochloride. After evaporating for some time on the sand bath and cooling, no crystals separated. The solution was evaporated further and allowed to stand four days over sulphuric acid, when a crop of crystals separated as long, thick needles. These crystals in mass had a dark green color; the dry powder was a lighter green in color. This sample was analyzed. No water was given off on heating the salt.

Solution in the Ratio of 3 : 1.—A solution of this ratio gave on cooling a crop of the hexaniline chloroferrate. The mother liquor on standing over sulphuric acid for a week gave a crop of long, thick needles, which, after drying, appeared to be the same green salt that was obtained from the 2 : 1 solution. Not enough of the salt was obtained for analysis.

Solution in the Ratio of 4 : 1.—A solution was made by adding 2.4 grams of aniline hydrochloride to 32 cc. of a solution of ferric chloride, containing 12 grams of ferric chloride, and

diluting slightly with hydrochloric acid. A green precipitate was formed which was filtered off through glass wool, and the solution was cooled, but no salt separated. After further concentration crystals separated on cooling as long plates 1–2 cm. in length. They had a resinous brown color; the dry powder was green. On standing over sulphuric acid a second crop of crystals, which looked black in solution, separated. On drying they were found to be long, thin, brownish green plates. There was also a crop of ferrous chloride.

The analysis of this second crop and of the salt from the 2 : 1 solution gave the following results:

	Calculated for $FeCl_3.2C_6H_5NH_3Cl$	Found Salt from Solution 4 : 1	2 : 1
Chlorine	42.04	41.87	41.85
		42.07	42.95
Iron	13.30	13.06	...
		13.36	13.34

This salt seemed to change its crystalline form according to the conditions of formation. When it was obtained by cooling a hot concentrated solution the plates separated with the brown color. By slow evaporation of the solution over sulphuric acid, the salt was deposited in needles or prisms. The salt is very soluble in weak hydrochloric acid and in water. Some specimens also showed a tendency to take up water on standing.

Hydrous Dianiline Chloroferrate,

$FeCl_3.2C_6H_5NH_3Cl.H_2O$

A solution in the ratio of 4 : 1 was prepared by adding 18 cc. of concentrated hydrochloric acid to 32 cc. of a solution of ferric chloride, which contained 12 grams of ferric chloride, and dissolving in this 2.4 grams of aniline hydrochloride. From the solution, a crop of long, thin needles was obtained. In solution these looked black, but in dry condition they were green. Two and seven-tenths grams of the salt were obtained.

The results of the analysis are the following:

	Calculated for $FeCl_3.2C_6H_5NH_3Cl.H_2O$	Found
Chlorine	40.32	40.26
Iron	12.75	12.60

Hexaniline Chloroferrate,

$FeCl_3.6C_6H_5NH_3Cl$

The preliminary work on this salt was entirely unsuccessful, owing to the oxidation of the aniline hydrochloride, as above mentioned. The salt can be obtained only from strongly acid solutions. It is a beautifully crystalline salt of an orange color, though the color changes with the crystalline habit: and this is dependent on the conditions. This was seen, also, in the case of the dianiline chloroferrate. It is obtained from some solutions in yellow silky needles, either parallel or radiating from a point. By slow cooling or by evaporation over sulphuric acid, it is formed in prisms or heavy needles crystallizing in bunches, where the crystals cross each other in the middle, giving a very beautiful appearance.

The salt is very soluble in water, alcohol and dilute acids; but it is decomposed at the same time, since the ferric chloride oxidizes the aniline hydrochloride to form the blue precipitate previously described. The solutions of the salt in hydrochloric acid, of specific gravity about 1.12, range from light yellow in dilute solutions to blackish green in concentrated solutions, which have stood a short time. When the salt is dropped into a solution of sodium hydroxide, or better when such a solution is added to a solution of the salt in dilute hydrochloric acid, the aniline collects in drops on the surface, and the iron is precipitated as red ferric hydroxide. The dianiline chloroferrate acts similarly and the solutions of both salts give all the tests for ferric iron.

This salt was obtained from solutions of ferric chloride and aniline hydrochloride in all the ratios of 3 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 8. In the 3 : 1 and 2 : 1 solutions either this or the dianiline chloroferrate may separate; or first, a crop of the hexaniline chloroferrate may separate and then, from the mother liquor, a crop of the dianiline salt may be deposited, as above described.

Solution in the Ratio of 3 : 1.—Twenty-four cc. of a solution of ferric chloride, containing 9 grams of ferric chloride, was diluted with 10 cc. of concentrated hydrochloric acid, and in it was dissolved 2.4 grams of aniline hydrochloride. The solution, on standing, deposited a bunch of long, yellow needles.

Another solution in the ratio of 3 : 1 was made, which contained 6 grams of ferric chloride and 1.6 grams of aniline hydrochloride. A crop of yellow, fine, silky needles was deposited fron the solution.

Both of these salts were analyzed with the following results:

	Calculated for $FeCl_3.6C_6H_5NH_2Cl$	Found	
		First preparation	Second preparation
Chlorine	33.94	34.38	35.27
Iron	5.96	6.47	6.48

Solution in the Ratio of 2 : 1.—Sixteen cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, was added to 18 cc. of concentrated hydrochloric acid, and in this was dissolved 2.4 grams of aniline hydrochloride. On cooling this solution, a crop of fine, silky crystals of a brownish yellow color separated. One and five-tenths grams of the salt were obtained.

Solution in the Ratio of 1 : 1.—A solution was made by mixing 16 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, with 18 cc. of concentrated hydrochloric acid and adding 4.8 grams of aniline hydrochloride. From this solution 3.1 grams of a salt was obtained in the form of fine, silky needles, which in the solution had a golden yellow color. The results of the analyses of these salts were the following:

	Calculated for $FeCl_3.6C_6H_5NH_2Cl$	Found for salt from	
		Solution 2 : 1	Solution 1 : 1
Chlorine	33.94	33.44	33.48
Iron	5.96	6.38	6.10

No water was given off on heating the salt from the 2 : 1 solution; the salt from the 1 : 1 solution was not tested.

Solution in the Ratio of 1 : 2.—A solution of 16 cc. of ferric chloride, equal to 6 grams of ferric chloride, was added to 20 cc. of concentrated hydrochloric acid, and 9.6 grams of ani-

line hydrochloride was dissolved in it. It was difficult to dissolve all the aniline hydrochloride; so the solution was further diluted to keep all the double salt dissolved. Six and forty-seven hundredths grams of the salt separated, on cooling, in larger needles than those obtained from the preceding solutions. They were also of a darker yellow color when in the solution, and when dried they had a brownish tint.

Solution in the Ratio of 1 : 4.—A solution containing 3 grams of ferric chloride and 9.5 grams of aniline hydrochloride was made up with hydrochloric acid to a volume of 50 cc. On cooling the salt separated in yellow needles. The analyses of these salts gave the following results:

	Calculated for $FeCl_3.6C_6H_5NH_2Cl$	Found for salt from Solution 1 : 2	Found for salt from Solution 1 : 4
Chlorine	33.94	34.64	33.45
			33.50
Iron	5.96	5.61	6.03
			6.19

The salt was best obtained from a solution in the ratio of 1 : 4 as follows: Eleven and six-tenths cc. of a solution of ferric chloride, containing 3 grams of ferric chloride, was diluted to 75 cc. with hydrochloric acid—three parts of concentrated acid to one part water—and in it was dissolved 9.4 grams of aniline hydrochloride. The solution was heated on a water bath, when it turned a deep brownish red and remained perfectly clear. The salt crystallized in needles and prisms, which had a yellow color when viewed on the side, but when viewed on the ends they showed a decided red color. The dry salt in coarse powder had a reddish yellow color, but in fine powder it was a pure yellow. Six grams of the crystals were obtained.

Another preparation of the salt was made just as above. Part of the salt was dried and prepared for analysis; a second part was recrystallized from concentrated hydrochloric acid. The recrystallized salt formed, like that from the first 1 : 4 solution, in needles crossing each other in the middle. The mother liquor from this specimen, on standing over sulphuric acid, gave a crop of single needles starting at the surface of the liquid and extending down through the solution.

The three portions gave these results on analysis:

	Calculated for $FeCl_3.6C_6H_5NH_3Cl$	Uncrystallized	Found Recrystallized 1st crop	Found Recrystallized 2nd crop
Chlorine	33.94	33.39 33.80	33.76	33.83
Iron	5.96	6.09 6.29	6.12	
Nitrogen	8.95	8.41 8.45		
		No water given off on heating		No water given off on heating

Solution in the Ratio of 1 : 8.—A solution was prepared containing 3 grams of ferric chloride and 19.1 grams of aniline hydrochloride. The salt prepared in yellow crystals as fine needles and in prisms which frayed off on the ends into long, fine needles. These prisms cross in the middle.

The results of the analyses were the following:

	Calculated for $FeCl_3.6C_6H_5NH_3Cl$	Found
Chlorine	33.94	33.64 33.78
Iron	5.96	5.94 5.90

The salt gave off no water on heating to 100°.

Very fine specimens of the hexaniline chloroferrate were obtained from solutions of ferrous chloride and aniline hydrochloride during the work on the salts formed by the action of ferrous chloride on aniline hydrochloride. On exposure to the air the ferrous chloride became oxidized to ferric chloride which in the presence of excess of aniline hydrochloride formed the higher salt. In one case a specimen of the *dianiline* chloroferrate was obtained. The addition of a little hydrogen peroxide to the solution of the ferrous compounds also produced the hexaniline chloroferrate.

The crystalline form of the salt obtained thus was the same as when obtained from ferric chloride directly.

Analyses of some samples obtained thus gave the following results:

	Calculated for $FeCl_3.6C_6H_5NH_3Cl$	Found I	Found II	Found III
Chlorine	33.94	33.83	33.44	33.60
		33.68	33.44	33.50
Iron	5.96	6.49	6.19	6.66
			6.23	6.46

Hydrous Hexaniline Chloroferrate

$FeCl_3.6C_6H_5NH_3Cl.2H_2O$

A solution of ferrous chloride and aniline hydrochloride in the ratio 2 : 1 had stood in contact with the air until it contained a large quantity of the orange *ferric* salt, the hexaniline chloroferrate. This was filtered off and recrystallized from concentrated hydrochloric acid.

On analysis it gave the following results:

	Calculated for $FeCl_3.6C_6H_5NH_3Cl.2H_2O$	Found
Iron	32.70	32.73
		32.80
Chlorine	5.74	5.78
		5.82

A second crop from the mother liquor gave analyses for the anhydrous salt. The results are given under the hexaniline chloroferrates, from ferrous chloride and aniline hydrochloride, No. I. An attempt was made to obtain the hydrous salt by recrystallizing the hexaniline chloroferrate, obtained from a solution of ferric chloride and aniline hydrochloride, from concentrated hydrochloric acid, but the *anhydrous* salt was obtained.

Hexa-o-toluidine Chloroferrate,

$$FeCl_3.6C_6H_4\begin{matrix}CH_3\\ \diagdown\\ \diagup\\ NH_3Cl.3H_2O\end{matrix}$$

The first attempts to obtain double salts with ferric chloride and *o*-toluidine hydrochloride were not satisfactory, owing to the easy oxidation of the toluidine hydrochloride by the ferric chloride.

A solution of ferric chloride and *o*-toluidine hydrochloride

in hydrochloric acid, part dilute acid and part concentrated acid, was made in the ratio of 1 : 1. It was heated to boiling, when a dark tarry oil separated. The solution was evaporated to about one-half and cooled, when a crystalline substance separated. The mother liquor, on standing over sulphuric acid, gave a crop of crystals in the form of needles having a brownish yellow color, and arranged in clusters.

Another solution in the ratio of 1 : 1, and a solution in the ratio of 2 : 1 were prepared. From these, however, only a slight amount of the double salt was obtained, mixed with tarry decomposition products. Ferrous chloride was also deposited. Most of the action in both solutions was the oxidation of the *o*-toluidine hydrochloride.

A solution nearly in the ratio of 1 : 1 was made from 17 cc. of a solution of ferric chloride, containing 6.4 grams ferric chloride, and 5.27 grams of *o*-toluidine hydrochloride in 34 cc. of dilute hydrochloric acid and 10 cc. of the concentrated acid. The solution, on heating, became first deep red, then quite black, and began to decompose. It was boiled about two hours, filtered and cooled; after a time, a crop of a salt separated. The salt formed a bunch of needles, which started to crystallize at a point on the side of the beaker and nearly filled the solution. Three and forty-seven hundredths grams of the reddish yellow salt were obtained.

Another solution in the ratio of 1 : 1, containing 6 grams of ferric chloride and 5.27 grams of *o*-toluidine hydrochloride, were made up with 10 cc. of dilute acid and 5 cc. of the concentrated acid. The solution was heated to boiling for about half an hour, when there was a slight oxidation of the *o*-toluidine hydrochloride. After filtering the hot solution and letting it cool, the salt filled the solution so that the beaker could be turned upside down without spilling the liquid. Four and forty-two hundredths grams of the salt were obtained. On drying between filter paper in the press the edges of these two samples turned green.

Analyses of the samples give the following results:

	Calculated for $FeCl_3.6C_6H_4\begin{matrix}CH_3\\NH_3Cl\end{matrix}.3H_2O$	Found 1st sample	2nd sample	3rd sample
Chlorine	29.59	29.24	30.29	29.12
				29.22
Iron	5.20	5.20	5.02	5.04
			5.34	5.18

In other solutions in different ratios there was not so much success in the work; more of the oxidation product was formed.

New Method of Preparation.—It was thought that the double salt might be obtained from solutions of ferric chloride and *o*-toluidine hydrochloride dissolved in dilute hydrochloric acid of specific gravity 1.12, by saturating the solution with hydrochloric acid gas. This was tried with such success that it was used in all the subsequent work.

By this method the hexa-*o*-toluidine chloroferrate was obtained from solutions of ferric chloride and *o*-toluidine hydrochloride in ratios of 4 : 1, 2 : 1, 1 : 1, 1 : 4, 1 : 8 and 1 : 12. The salt could be recrystallized from concentrated hydrochloric acid by saturating the warm acid with the salt, and allowing the solution to cool; or by nearly saturating weak, cold hydrochloric acid with the salt and passing into the solution hydrochloric acid gas nearly to saturation. On trying to crystallize the salt from dilute acid it was decomposed and toluidine hydrochloride separated. In solution in water and in ethyl alcohol the salt decomposed into its constituents, which then reacted to form the oxidation product. Ethyl ether decomposed the salt, leaving a white solid. The crystals of the salt formed in best shape by slow evaporation of the strong hydrochloric acid solution over sulphuric acid and solid potassium hydroxide.

Solution in the Ratio of 4 : 1.—To 21 cc. of a solution of ferric chloride, containing 8 grams of ferric chloride, 1.77 grams of *o*-toluidine hydrochloride was added. The solution was prepared cold and allowed to stand about an hour and a half, during which time—the solution not being strongly acid—the substances had reacted so that the solution became green. This shows the ease with which ferric chloride acts on *o*-toluidine hydrochloride. The beaker containing the solution

was placed in cold water while hydrochloric acid gas was passed into it. After filtering the solution it was allowed to stand overnight, when a crop of the salt separated in reddish yellow needles crystallizing in bunches.

Solution in the Ratio of 2 : 1.—Thirty-two cc. of a solution of ferric chloride, containing 12 grams of ferric chloride and 5.27 grams of *o*-toluidine hydrochloride, gave a deposit of an amorphous powder when the cold solution was saturated with hydrochloric acid gas. This powder was filtered off and recrystallized by dissolving in hydrochloric acid—one-half concentrated acid to one-half dilute acid—and saturating the solution with hydrochloric acid gas. After standing four days over sulphuric acid, 2.5 grams of the needles were obtained.

Solution in the Ratio of 1 : 1.—To 16 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, 5.27 grams of *o*-toluidine hydrochloride were added, which did not all dissolve. The solution was nearly saturated with the hydrochloric acid gas. It became heated on absorbing the gas so that on cooling the salt separated in good condition.

The results of the analyses of these salts were the following:

	Calculated for $FeCl_3.6C_6H_4\begin{matrix}CH_3\\ \\ NH_3Cl.3H_2O\end{matrix}$	Found for salt from Sol. 4 : 1	Sol. 2 : 1	Sol. 1 : 1
Chlorine	29.59	29.69	29.33	29.41
		29.69	29.31	29.43
Iron	5.20	5.76	5.42	5.83
		5.47	5.19	....

Solution in the Ratio of 1 : 4.—To 20 cc. of hydrochloric acid—1 part dilute acid to 1 part concentrated acid—1 gram of ferric chloride and 3.536 grams of *o*-toluidine hydrochloride were added. On saturating with hydrochloric acid gas the solution became nearly solid with the salt which separated. The salt was filtered off and as much of the liquid as possible was separated by use of the filter pump. The salt was divided into three parts: Part I was prepared for analysis without recrystallization; Part II was recrystallized by saturating hot concentrated acid with the salt and cooling; Part III was recrystallized by dissolving in the dilute acid and saturating

the solution with the gas. There was not enough of the salt, from Part II, for the determination of both iron and chlorine. The results of the analyses are as follows:

	Calculated for $FeCl_3.6C_6H_4\langle^{CH_3}_{NH_3Cl}.3H_2O$	Found Part I	Part II	Part III
Chlorine	29.59	29.52	29.49	29.76
Iron	5.20	5.12	...	5.64

Solution in the Ratio of 1 : 8.—Two and seven-tenths cc. of a solution of ferric chloride—containing 1 gram of ferric chloride—was diluted to about 35 cc. with hydrochloric acid and 7.07 grams of *o*-toluidine hydrochloride were added. On saturating with hydrochloric acid gas the solution became nearly solid from the separation of the salt. About two-thirds of this solid mass was heated to 40° with 75 cc. of concentrated hydrochloric acid; on cooling *o*-toluidine hydrochloride separated. This was filtered off and from the filtrate the reddish yellow needles were obtained.

Solution in the Ratio of 1 : 12.—One gram of ferric chloride in solution and 10.609 grams of *o*-toluidine hydrochloride were dissolved in 40 cc. of concentrated hydrochloric acid. The solution was cooled and hydrochloric acid gas passed in, when on standing overnight both *o*-toluidine hydrochloride and the double salt crystallized out. By fractional crystallization the double salt was obtained pure.

The analyses of these samples gave these results:

	Calculated for $FeCl_3.6C_6H_4\langle^{CH_3}_{NH_3Cl}.3H_2O$	Found for salt from Sol. 1 : 8	Sol. 1 : 12
Chlorine	29.59	29.60	29.69
Iron	5.20	5.65	...

A sample of the salt from the 1 : 8 solution was heated at 95°–100°, when it gave off water. When heated to 125° it was found that *o*-toluidine hydrochloride had sublimed.

The hexa-*o*-toluidine chloroferrate was obtained also by oxidation of solutions of ferrous chloride and *o*-toluidine hydrochloride on exposure to the air. When it was attempted to obtain second crops of crystals from solutions of the fer-

rous chloride and toluidine hydrochloride the *ferric* double salt separated. Two samples of second crops of crystals from solutions of ferrous chloride and *o*-toluidine hydrochloride in the ratios 2 : 1 and 3 : 1 gave, on analysis, the following results:

	Calculated for $FeCl_3.6C_6H_4\begin{matrix}CH_3\\NH_3Cl\end{matrix}.3H_2O$	Found for salt from Sol. 2 : 1	Found for salt from Sol. 3 : 1
Chlorine	29.59	29.25	29.36
Iron	5.20	5.95	5.35

Many attempts were made to prepare double chlorides of ferric chloride and *o*-toluidine hydrochloride containing a larger proportion of ferric chloride, but without success. Solutions in the ratio of 8 molecules of ferric chloride to 1 molecule of *o*-toluidine hydrochloride were made from 21 cc. of a solution of ferric chloride—containing 8 grams of ferric chloride—and 0.884 gram of dry *o*-toluidine hydrochloride. When these solutions were saturated in the cold, with gaseous hydrochloric acid, a little of a salt that seemed to be hexa-*o*-toluidine, chloroferrate, separated, but quickly dissolved. No salt could then be obtained from the solution even on cooling in ice water. On heating the solutions in order to concentrate them, the *o*-toluidine hydrochloride was destroyed, no matter how acid the solution had been made.

Attempts were also made to obtain a salt from a very nearly saturated solution of ferric chloride containing 8 grams of ferric chloride, to which was added 0.884 gram of *o*-toluidine hydrochloride, by saturating with the gaseous acid, and cooling in ice water, but without success.

Di-m-toluidine Chloroferrate,

$$FeCl_3.2C_6H_4\begin{matrix}CH_3\\NH_3Cl\end{matrix}$$

This salt separated from concentrated solutions of ferric chloride and *m*-toluidine hydrochloride in the ratio of four molecules of ferric chloride to one molecule of *m*-toluidine hydrochloride, 3 : 1, 2 : 1, 1 : 4 and 1 : 6, in shining, yellow plates when gaseous hydrochloric acid was passed into the solution.

The salt was deliquescent and could not readily be obtained in condition for analysis.

	Calculated for $FeCl_3.2C_6H_4\langle^{CH_3}_{NH_3Cl}$	Found for salt from Sol. 1 : 1	Sol. 1 : 4	Sol. 4 : 1
Chlorine	39.42	38.75	38.74	38.40
Iron	12.47	12.31	12.46	12.90

Tri-m-*toluidine Chloroferrate*,

$$FeCl_3.3C_6H_4\langle^{CH_3}_{NH_3Cl}$$

This salt could not be obtained in very satisfactory condition; only one specimen was obtained pure enough for analysis. When solutions in the ratios 1 : 3, 1 : 4 and 1 : 6 were saturated with hydrochloric acid gas, first the lower salt separated; but, on continued action of the acid, the lower salt changed its crystalline form and the higher salt was produced.

Solution in the Ratio of 1 : 3.—To a solution of 2.643 grams of *m*-toluidine hydrochloride in 6.2 cc. of dilute hydrochloric acid was added 3.88 cc. of a solution of ferric chloride containing 1 gram of ferric chloride. The beaker containing the solution was placed in cold water and hydrochloric acid gas was passed into it. When the oil separated the beaker was placed in crushed ice while the saturation with the gaseous acid continued. The solution cleared up and then crystals separated in two forms; all through the solution were yellow plates as in the 1 : 4 solution, then there were bunches of green crystals. These were all broken up with the stirring rod and 2.5 cc. of dilute hydrochloric acid were added. On continued absorption of hydrochloric acid gas the crystals changed form and the yellow plates were replaced by finer crystals of a lighter yellow color. When the change seemed to be complete, the mass—which looked like hexa-*o*-toluidine chloroferrate as it separated from concentrated solution—was filtered off.

The salt formed a sticky mass fuming with hydrochloric acid. It was very difficult to prepare for analysis, being deliquescent and adhering to the drying paper. The salt which

was left, part of it having been dissolved by the moisture of the air and absorbed by the drying paper, was further dried in a desiccator.

Part of the salt before the final drying was dissolved in hot, concentrated hydrochloric acid and the solution was cooled in ice water. The salt which separated was the di-*m*-toluidine chloroferrate.

The analysis of the dried salt gave the following results:

Chlorine	35.61
Iron	10.17

The ratio of the iron to the chlorine in the salt was 1 : 5.54. Taking the ratio as 1 : 6 the salt must have been the tri-*m*-toluidine chloroferrate, for which the calculated percentages are: Chlorine, 35.85; iron, 9.45.

A second solution in the ratio of 1 : 3 was prepared which contained the same amounts of toluidine hydrochloride and of ferric chloride, but whose volume was 15 cc. This gave first the di-*m*-toluidine chloroferrate. The continued action of the hydrochloric acid gas produced the same change as before, but the substance which separated seemed to be a mixture of the two salts.

The ratio of the constituents was changed to 1 : 6 by the addition of 2.643 grams of the toluidine hydrochloride in 9 cc. of hydrochloric acid. The solution was warmed to bring all the salts into solution. When it had been cooled and hydrochloric acid gas passed into it, the di-*m*-toluidine chloroferrate separated without the formation of the oil. This salt did not change over to the higher salt so far as could be seen. When the beaker was removed from the ice water most of the salt was dissolved.

A second solution in ratio of 1 : 6 was prepared containing 0.5 gram of ferric chloride and 2.643 grams of *m*-toluidine hydrochloride in 10 cc. of liquid. The di-*m*-toluidine salt separated first, then some of the lighter fine crystals appeared, which seemed to be composed of fine needles. After one to two hours all the crystals seemed to have changed over to this form.

All attempts to get this crop of crystals in condition for analysis failed. The mother liquor could not be entirely separated by the use of the filter pump, and the solution was so strongly acid that the drying paper was disintegrated and mixed with the salt, so that they could not be separated. No further attempts to prepare this salt were made.

Tri-p-*toluidine Chloroferrate*,

$$FeCl_3.3C_6H_4\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ NH_3Cl\end{matrix}$$

The first part of the work with ferric chloride and *p*-toluidine hydrochloride was very unsatisfactory. Solutions were made in the ratio of 1 : 1 and 1 : 4. From solutions in the ratio 1 : 4 only *p*-toluidine hydrochloride separated. From the solutions in the ratio 1 : 1 a salt was obtained in good shape; but on standing over sulphuric acid this broke down into its constituents.

It was thought from some previous work on ferrous chloride with *o*-toluidine hydrochloride that the union of the two chlorides might be facilitated by keeping the solution at the boiling temperature for a long time, but the preliminary work showed that this did not hold for ferric chloride and *p*-toluidine hydrochloride. This showed, also, that the double salt cannot exist except in strongly acid solution, and that the ferric chloride acts on *p*-toluidine hydrochloride much less than it does on *o*- and on *m*-toluidine hydrochloride.

Tri-*p*-toluidine chloroferrate was obtained from solutions of ferric chloride and *p*-toluidine hydrochloride in ratios of 2 molecules of ferric chloride to 1 of *p*-toluidine hydrochloride, of 3 : 1 and of 6 : 1. The salt separated from the solutions in lustrous red crystals whose form varied somewhat with the conditions of its preparation. In some cases it was obtained as plates, in other cases as thick prisms.

Solution in the Ratio of 2 : 1.—To 0.881 gram of *p*-toluidine hydrochloride dissolved in 15 cc. of dilute hydrochloric acid were added 3.1 cc. of a solution of ferric chloride, containing 2 grams of ferric chloride. The warm solution was treated

with hydrochloric acid gas, when *p*-toluidine hydrochloride separated. It was then placed in ice water and the gas passed through the solution, but the salt did not separate. Thinking that the temperature might be too low, the solution was heated and the gaseous acid was passed in while the solution cooled. A double salt separated, but *p*-toluidine hydrochloride was mixed with it. From the mother liquor a double salt separated in short prisms with lustrous faces. As they were free from *p*-toluidine hydrochloride they were prepared for analysis.

Solution in the Ratio of 3 : 1.—A solution was prepared containing 6 grams of ferric chloride and 1.76 grams of *p*-toluidine hydrochloride in 40 cc. of dilute hydrochloric acid. The solution was heated to boiling and the hot, nearly opaque, red solution was treated with hydrochloric acid gas until it was strongly acid. It was then cooled and more of the gas passed into it. The absorption of the gas produced much heat. At first *p*-toluidine hydrochloride separated; this was then changed to the double salt. The salt was filtered off, when it was seen to be composed of reddish yellow plates. In fine powder the salt was of a darker color than were some of the specimens previously obtained.

The analyses of these salts gave the following results:

	Calculated for $FeCl_3.3C_6H_4\begin{cases}CH_3\\NH_3Cl\end{cases}$	Found for salt from Sol. 2 : 1	Found for salt from Sol. 3 : 1
Chlorine	35.85	35.55	35.60
Iron	9.45	9.27	9.43
Nitrogen	7.04	...	6.80
Water	0.0	....	0.0

The salt from the 3 : 1 solution when heated at 110°–115° gave off no water, but a sublimate of toluidine hydrochloride was formed.

Solutions in the Ratio of 6 : 1.—To 9.3 cc. of a solution of ferric chloride, containing 6 grams of ferric chloride, was added 0.881 gram of *p*-toluidine hydrochloride. The solution was warmed slightly and hydrochloric acid gas was passed into it, when it became hot. The beaker was then placed in cold water

while the saturation with the hydrochloric acid gas was continued. The solution was left overnight, when a crop of the red salt separated. This was prepared for analysis.

A second solution was made up like the last except that it was diluted with 10 cc. of dilute hydrochloric acid. The solution was saturated with hydrochloric acid gas as it cooled to near 0° in ice water, when a crop of the salt separated.

The results of the analyses of these samples of the salt were the following:

	Calculated for $FeCl_3.3C_6H_4\begin{matrix}CH_3\\NH_2Cl\end{matrix}$	Found for salt from First sol.	Found for salt from Second sol.
Chlorine	35.85	35.64	36.16
Iron	9.45	9.36	10.01

Salts from Ferrous Chloride and the Hydrochlorides of Aniline and o-Toluidine

Solutions of ferrous chloride and aniline hydrochloride in the ratios of 3 : 1, 2 : 1, 1 : 1, 1 : 2, in slightly acid solutions, gave mixtures of aniline hydrochloride in plates, nearly white or light yellow crystals in short needles, and, often mixed with these, red crystals in thicker, longer needles than the yellow ones. Then it was found that the solutions which were filtered hot in contact with the air or which stood for a long time exposed to the air gave a larger proportion of the red crystals. A sample of these, which was obtained free from the light yellow needles, gave the ordinary reactions of iron in the *ferric* state. The salt was analyzed and it proved to be hexaniline *chloroferrate*.

	Calculated for $FeCl_4.6C_6H_5NH_2Cl$	Found
Chlorine	33.94	33.53
Iron	5.96	6.80

The light yellow needles, when freshly prepared and quickly freed from the mother liquor, were nearly white, but they became slightly yellow before they could be filtered in quantity from the mother liquor. They gave all the reactions for iron in the ferrous state. The best test was the formation of the ferrous hydroxide and its instantaneous change to the red ferric hydroxide when hydrogen peroxide was added.

It was also found that a slightly acid solution of the ferrous chloride and aniline hydrochloride, which had deposited the aniline hydrochloride, gave a good yield of the light yellow needles when concentrated hydrochloric acid was poured into the solution. The change of the plates of aniline hydrochloride over to the needles of the double salt wherever the strong acid came in contact with them was very interesting to watch. It was then found that by using quite strongly acid solutions the ferrous double salt could be obtained, on the first cooling of the solution, free from the ferric salt. A sample of the light yellow crystals on analysis gave results that pointed to the formula $FeCl_2.2C_6H_5NH_3Cl.2H_2O$ for the salt.

	Calculated for $FeCl_2.2C_6H_5NH_3Cl.2H_2O$	Found
Chlorine	33.58	33.23 32.89
Iron	13.28	14.44 15.03

Dianiline Chloroferrite,

$FeCl_2.2C_6H_5NH_3Cl.2H_2O$

The salt was obtained from solutions containing all proportions of ferrous chloride and aniline hydrochloride, from 1 : 4 to such a ratio that ferrous chloride separated from the solution mixed with the double salt. In a series of experiments four solutions were made up in the ratios 4 : 1, 3 : 1, 2 : 1 and 1 : 1.

Solution in the Ratio of 4 : 1.—This solution contained 8.72 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 50 cc. of liquid. It was heated to boiling for a time, but on cooling no salt separated. When it was placed in snow a crop of the light yellow needles separated. By the next morning a second crop of the salt had formed at the ordinary temperature. The salt was filtered off and prepared for analysis.

Solution in the Ratio of 3 : 1.—This solution contained 6.54 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 39 cc. of liquid. The solution was boiled a short time and then cooled, when the light yellow salt separated at

ordinary temperatures. This was filtered off and prepared for analysis. The next morning a second crop of the salt had formed, but it was mixed with crystals of ferrous chloride.

Solution in the Ratio of 2 : 1.—This solution was composed of 4.36 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 29 cc. of liquid. After boiling and cooling, the solution deposited about twice as much of the light yellow crystals as did the 3 : 1 solution. This crop of the salt was prepared for analysis. The second crop of the salt in this case also contained crystals of the ferrous chloride.

Solution in the Ratio of 1 : 1.—The solution contained 2.18 grams of ferrous chloride and 2.22 grams of aniline hydrochloride in 19 cc. of liquid. The solution was boiled and then allowed to cool, when it became nearly solid with the salt which had separated. The salt was dissolved by the addition of dilute hydrochloric acid and heating; it was then left overnight, when there was a crop of the light yellow crystals mixed with some of the red ferric salt. These were separated mechanically and the ferrous salt was prepared for analysis. The analyses of these crops gave the following results:

	Calculated for $FeCl_2.2C_6H_5NH_2Cl.2H_2O$	Found for salt from Sol. 4 : 1	Sol. 3 : 1.	Sol. 2 : 1	Sol. 1 : 1
Chlorine	33.58	33.75	33.91	33.61	33.66
		33.86	33.76	33.15	
Iron	13.28	14.12	13.31	14.16	...
			13.86	14.26	

The solution was made in the ratio of 1 : 2.5, which contained 13.68 grams of ferrous chloride and 32.9 grams of aniline hydrochloride in 183 cc. of solution. The solution was only slightly acid, so that on boiling and cooling only aniline hydrochloride separated. About one-half the volume of concentrated hydrochloric acid was added; the solution was then heated and allowed to cool, when the light yellow ferrous salt separated in large quantity. This was filtered off and prepared for analysis, the results of which were as follows:

	Calculated for $FeCl_2.2C_6H_5NH_2Cl.2H_2O$	Found
Chlorine	33.58	33.88
Iron	13.28	13.25

From the mother liquor more of the salt crystallized. This was left in the solution, when after two days the ferric salt appeared all through the mass. After standing some weeks the change to the ferric double salt seemed to be complete. This salt gave on analysis results agreeing with those required for the hexaniline chloroferrate.

The dianiline chloroferrite when heated in the air bath at 90° turned nearly black, and when this residue was dissolved in water a dark solution was obtained with some insoluble substance; the salt is therefore decomposed on heating even at 90°.

When allowed to stand in the sulphuric acid desiccator the salt loses weight, but, as before stated, in treating of the methods of analysis, the percentage of water could not be determined.

After remaining in the specimen tube a short time—a few weeks—these ferrous salts become green and show other signs of decomposition.

Tri-o-toluidine Chloroferrite,

$$FeCl_2.3C_6H_4\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ NH_3Cl.6H_2O\end{matrix}$$

This salt was obtained only once when the analyses were reliable, though the analyses of another preparation pointed to the same salt with more water of crystallization. In all subsequent work the salt to be described later was obtained.

Three solutions were prepared. The first solution, in the ratio of 1 : 1, was composed of 10 cc. of a saturated solution of ferrous chloride, containing 4 grams of ferrous chloride, and a nearly saturated solution of 4.5 grams of *o*-toluidine hydrochloride. This solution, when heated and then allowed to cool, gave only *o*-toluidine hydrochloride.

The second solution, in the ratio of 2 : 1, was made by mixing 20 cc. of the saturated solution of ferrous chloride with a saturated solution of 4.5 grams of *o*-toluidine hydrochloride. From this ferrous chloride separated first; then a double salt. The double salt was dissolved by warming the solution and pouring off from the crystals of ferrous chloride.

From the liquid a crop of yellow crystals separated in long, fine needles. The analyses of this sample did not give concordant results.

The third solution was composed of 12 grams of ferrous chloride in saturated solution and 4.5 grams of *o*-toluidine hydrochloride in saturated solution. This first gave ferrous chloride, then the mother liquor gave a mixture of the yellow needles, as obtained in the previous solution, with toluidine hydrochloride and crystals of a different yellow color.

Solution in the Ratio of 1 : 1.—As it was thought that these solutions did not contain enough acid, a second solution, in the ratio of 1 : 1, was prepared thus: Ten cc. of the saturated solution of ferrous chloride, containing 4 grams of ferrous chloride, was added to a solution of 4.5 grams of *o*-toluidine hydrochloride in 15 cc. of concentrated hydrochloric acid and 5 cc. of water. The solution was heated, and, when it was cooled, a crop of crystals formed which, when viewed on the ends, had a reddish yellow color, but, when viewed on the side, were of a light yellow color. Three grams of the dry salt were obtained. On analysis the salts gave the following results:

	Calculated for $FeCl_2.3C_6H_4\langle^{CH_3}_{NH_3Cl.6H_2O}$	Found
Chlorine	26.62	26.36 26.68
Iron	8.42	8.00 8.37

Hexa-o-toluidine Chloroferrite,

$$FeCl_2.6C_6H_4\langle^{CH_3}_{NH_3Cl.xH_2O}$$

From solutions of ferrous chloride and *o*-toluidine hydrochloride in ratios varying from 2 : 1 to 1 : 4, ferrous chloride, toluidine hydrochloride and a double salt may separate, according to the condition of the experiment. In many cases a mixture of any two, or of all three of the substances, may be obtained. The analyses of the double salt—when the purity

of the salt could be relied upon—in all cases, except the one already given, pointed to the compound of the formula

$$FeCl_2.6C_6H_4\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ NH_3Cl.xH_2O\end{matrix}$$

In the first part of this work the solutions containing ferrous chloride and toluidine hydrochloride were boiled and cooled in beakers exposed to the air, so that, where there were second or third crops obtained from the mother liquors, these were found to be the *hexa-o-toluidine chloroferrate*, already described. Later the salt was made in an atmosphere of hydrogen.

Two solutions of ferrous chloride and *o*-toluidine hydrochloride were made up in the ratios of 2 : 1 and of 3 : 1. These solutions contained, respectively, 8 grams of ferrous chloride to 4.5 grams of *o*-toluidine hydrochloride, and 12 grams of ferrous chloride to 4.5 grams of *o*-toluidine hydrochloride; the volume was about 60 cc.

The 2 : 1 solution gave a crop of a double salt before the solution was quite cold. This was filtered off and prepared for analysis. Later a mixture of crystals of ferrous chloride and of a double salt was deposited.

The 3 : 1 solution gave a crop of the double salt that seemed to be free from impurities. It was analyzed.

A second solution in the ratio of 3 : 1 was made like that above; from this solution a salt was obtained. The analyses of these salts gave the following results:

	Found for salt from		
	Sol. 2 : 1	Sol. 3 : 1, No. I	Sol. 3 : 1, No. II
Chlorine	27.91	28.78	28.16
	27.92	28.77	28.14
		28.44	28.18
Iron	5.37	5.48	5.36
		5.42	5.39
Ratio of iron to chlorine	1 : 8.23	1 : 8.44	1 : 8.4

These salts gave ferrous hydroxide with potassium hydroxide.

Both of the mother liquors of the solutions in the ratio 3 : 1

gave crops of an orange salt, which, on analysis, proved to be hexa-*o*-toluidine chloroferrates.

In view of the results previously obtained in the investigation of double halides, this salt was entirely unexpected. Out of several hundred double halides that have been described this is the only one containing such a large proportion of the basic halide. Every effort was made to learn whether any deep-seated change takes place when ferrous chloride and *o*-toluidine are brought together, but the evidence all goes to show that the product is in fact a salt of the type $FeCl_2.6MCl$.[1]

REVIEWS

METHODS IN CHEMICAL ANALYSIS, Originated and Developed in the Kent Chemical Laboratory of Yale University. Compiled by FRANK AUSTIN GOOCH, Professor of Chemistry and Director of the Kent Chemical Laboratory in Yale University. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1912. pp. xii + 536. Price, $4.00.

In the words of the author: "The object of this volume is to present concisely the principal results reached by workers in the Kent Chemical Laboratory of Yale University in the investigation and development of methods in chemical analysis. In the account of processes, modified or original, only proved procedure and immediately related experimental data are, as a rule, given."

No one can fail to be deeply impressed with this magnificent record of the achievements of the investigators in the Kent Chemical Laboratory in the field of analytical chemistry under the leadership of the compiler. Besides descriptions of many laboratory appliances and methods of general procedure, one or more methods for the estimation of no less than forty-seven elements are discussed. These include nearly all the common elements as well as some rare ones. The skill with which the gist of each investigation has been selected and the clearness with which it has been presented, together with the wide field covered, make the book invaluable to any one who is frequently confronted with new analytical problems.

One hesitates to criticize so admirable a production, but at any rate it is permissible to suggest that in the references the

[1] Finding myself at present in a position to enable me to devote a large proportion of my time to chemical research, I am planning to review the whole subject of the double halides in the hope of getting further light upon the regularities in their composition, for, in spite of some irregularities, it is undoubtedly true that they show a strong tendency to conform to a few types as originally set forth by me in 1888 (THIS JOURNAL, 11, 291).—I. R.

date of publication would sometimes be of assistance. While it is true that progress in analytical chemistry is made largely in the laboratory by process of trial, and while frequently the principle of a method turns out to be less simple than appearances at first indicate, so that theory must be adapted to fit the facts, yet on reading this book one cannot help regretting at times that the results are not discussed from the standpoint of the modern theory of solution. GREGORY P. BAXTER

A COLLEGE TEXT-BOOK OF QUANTITATIVE ANALYSIS. By HERBERT RAYMOND MOODY, S.B. (M.I.I.), A.M., PH.D. (COLUMBIA), Associate Professor of Analytical and Applied Chemistry, College of the City of New York. New York: The Macmillan Co. 1912. pp. vi + 165.

This book is intended for beginners and discusses a limited number of the more common quantitative methods. The chief emphasis is laid upon mechanical processes, with the idea of saving as much as possible of the instructor's energies by preventing mistakes on the student's part. The directions are therefore very complete. The author also lays stress on the intelligent employment of time in quantitative analysis.

Unfortunately, the scientific treatment of the subject is less satisfactory. As examples of the defects to which the book is subject, the following may be cited: The student is led to infer that weights may be determined with an accuracy of 0.1 milligram, yet no mention is made of the necessity of using calibrated weights; the student is told to wipe a weighing tube before weighing; handling a weighing tube with the fingers is directly implied. One cannot but question the advisability of giving, as the first quantitative experiment, the manipulation of so troublesome a substance as aluminium hydroxide. In the determination of silica, only one evaporation and filtration is prescribed. The solubility of precipitates is inadequately discussed, and the statement that nitric acid diminishes the solubility of silver chloride is obviously incorrect. The treatment of the subject of indicators leaves much to be desired. While the Gooch crucible is mentioned, no experiment is given which involves its use, and the Méker burner is nowhere described. Not only is the question of significant figures not discussed, but the use of figures is such as to lead to confusion in the mind of the student. For instance, 0.3795 gram of copper oxide is shown to yield 0.30322 gram of copper; 0.2500 gram of iron requires 31.18 cc. of permanganate solution, whence 1 cc. of permanganate is equivalent to 0.0080 gram iron; the following equation also occurs: $37.10 \times 0.0265 = 0.98315$. On page 138 the method of calculation is needlessly involved and necessitates multiplying and dividing by the molecular weight of hydrochloric acid. GREGORY P. BAXTER

THE VOLATILE OILS. By E. GILDEMEISTER and FR. HOFFMANN. Second Edition, by E. GILDEMEISTER. Written under the Auspices of the Firm of Schimmel & Co., Miltitz near Leipzig. Authorized translation by EDWARD KREMERS, Madison, Wis. First Volume. With Two Maps and Numerous Illustrations. New York: John Wiley & Sons, Inc. 1913. pp. xii + 677. Price, $5.00.

This book is divided into two distinct parts, historical and descriptive, the first of which remains substantially as written by Hoffmann for the first edition. This portion, occupying 241 pages, begins with a general history, from the earliest times, of the production, transportation and use of perfumes and aromatic substances. This is followed by a history of 87 of the best-known individual oils. This section concludes with a history of extraction and distillation processes from the crude apparatus and methods of antiquity to the giant stills of modern times. This is well illustrated with cuts of the older apparatus and full-page halftone pictures of some of the new.

Of the descriptive portion, 275 pages are devoted to an orderly enumeration and description of the chemical individuals that have been identified in volatile oils, together with a few compounds, such as ionone and the artificial musks, that may be classed with these. The treatment, particularly in the case of the more important substances, is very thorough, including the structural formula, occurrence, physical properties, chemical transformations, and means of identification. References to the literature are freely given. This is followed by a description of the methods of proximate analysis of volatile oils. Elaborate tables are given for the rapid calculation of analytical results. Some recent data have been inserted in the translation, which is well done.

The book is readable and interesting to the general reader in chemistry, while it serves as a convenient and comprehensive manual for the worker in the field. As might be expected in a book emanating from a commercial laboratory, great prominence is given to methods and products of that laboratory. The uninformed reader might even conclude that there is only one firm of importance in the large field. The firm and the authors deserve the thanks of the chemical public for a useful book.

E. EMMET REID

PRINCIPLES OF AGRICULTURAL CHEMISTRY. By G. S. FRAPS, PH.D., Associate Professor of Agricultural Chemistry, Agricultural and Mechanical College of Texas; Chemist, Texas Experiment Station; State Chemist. Easton, Pa.: The Chemical Publishing Co.; London: Williams & Norgate. 1913. pp. 493. Price, $4.00.

In this book the author has aimed to present the fundamental principles of agricultural chemistry from the point of view "of

the chemist dealing with agricultural problems," also "to emphasize chemical methods of investigation, and to stimulate scientific habits of thought."

The matter which is presented is based upon a course of lectures given by the author for a series of years at the Agricultural and Mechanical College of the State of Texas. The book is divided into twenty-four chapters, two of which deal with the fundamental principles of plant nutrition and with the relation of the plant to the atmosphere. Ten chapters are devoted to the soil, embracing its origin, classification, water content, physical properties, chemical and physical composition, chemical changes, soluble constituents, active plant food, and its losses, gains and deficiencies. One chapter treats of farm manures, two of fertilizers, and two of the constituents and composition of plants. The closing chapters are given over to chemistry in its relation to animals, embracing one chapter each on digestion, and the calculation of feeding rations, and three chapters covering the fundamental chemical problems relating to animal nutrition.

The material in general is well arranged. The chapters on the origin, the physical character and the chemical constituents of soils will be found particularly valuable for students who have neither taken an extended course in the subject previously nor a course in elementary geology and mineralogy.

In the discussion of "soil deficiencies" the writer unfortunately cites certain experiments with ground limestone and burned lime, to show the superiority of the former, in which the burned lime was applied at the worst point in the rotation and in which lime was used in highly excessive amounts. He has thus created unintentionally an unwarranted prejudice against burned and slaked lime. The mass of material to be predigested by the author was obviously too great to permit him to make a careful individual analysis of all of the experiments cited.

In the chapter on the sources and composition of fertilizers the author has apparently neglected to mention, in making comparisons of prices of ready-mixed and home-mixed goods, the fact that the former are usually sold on long credit, often in less than ton lots, whereas the latter are often sold in carload lots for cash or on short credit, or if in small quantities essentially as bargain-counter transactions to insure the sale of other goods. Due attention should have been paid to the fact that under such conditions they do not bear their share of the "overhead" expenses. The chapter is replete, however, with most valuable suggestions concerning the pre-

cautions to be taken in the making of field experiments with fertilizers, and it contains much other most valuable matter.

The closing chapters give a very satisfactory review of the general subject of animal nutrition.

No attempt is made in this book to discuss exhaustively the various topics which are considered and this is left to special works on these subjects. It does nevertheless furnish to the student a splendid foundation for more extended study. The book meets this special need most admirably and it is also adapted to the large number of other readers who wish to secure a general survey of the field, without specializing particularly in any one direction. For the purposes which have been mentioned this book appears to be better adapted to American needs than any heretofore published in this country or in England. The author is to be congratulated on his timely and meritorious production, and the book will be cordially welcomed by all who are interested in agricultural progress in the United States.

H. J. WHEELER

CYANAMID, Manufacture, Chemistry and Uses. By EDWARD J. PRANKE, B.Sc. Easton, Pa.: The Chemical Publishing Co. 1913. pp. vi + 112. Price, $1.25.

This book deals with the discovery, manufacture, preparation, properties and storage of cyanamide, its decomposition in the soil, use as a fertilizer and in mixed fertilizers, and with other topics relating to the subject. The book contains a number of references, and some original work of the author. The subject is fully treated. The book can be recommended to those who desire to become familiar with the subject.

G. S. F.

A FOUNDATION COURSE IN CHEMISTRY FOR STUDENTS OF AGRICULTURE AND TECHNOLOGY. By J. W. DODGSON, B.Sc. (LOND.), Lecturer in Chemistry at University College, Reading, and J. ALLAN MURRAY, B.Sc. (EDIN.), Lecturer in Agricultural Chemistry at University College, Reading. With Diagrams. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1913. pp. x + 243. Price, $1.10.

This book is intended for students attending short courses in agriculture, for those taking education courses in hygiene and domestic economy, and in fact for all who take up the study of chemistry as a preliminary to some technical or commercial pursuit. The book devotes space both to inorganic and organic chemistry. It has chapters headed air, water, limestone, ashes, sand, clay, etc., organic matter, paraffins and their derivatives, coal tar, some common metals. The author states that the book is based upon courses of lectures

given during a number of years. It contains a large number of chemical reactions, and many structural formulas, including one for silicic acid. G. S. F.

THE POLYTECHNIC ENGINEER. Published annually by the STUDENTS OF THE POLYTECHNIC INSTITUTE OF BROOKLYN. Vol. XIII. 1913. pp. 138.

The students of the Brooklyn Polytechnic Institute have good reason to be proud of their Annual. The typography, illustrations and binding are all that could be desired. The present volume is dedicated to Professor Samuel Sheldon, of the Physics and Electrical Engineering Department. Of interest to chemists may be mentioned the articles on the Thickness of Films of Silver upon Glass, by Irving W. Fay and Arthur C. Rauchfuss; The Industries of Detroit, by John C. Olsen; Blue and Iridescent Gelatine-Copper, by Frederick W. Moe, Jr.; Chinese Wood Oil, by Everitt J. Cole; and Résumé of the Lectures delivered by Sir William Ramsay at the Institute on Oct. 22, 29, and Nov. 5, 1912. C. A. R.

LOGARITHMIC REDUCTION TABLES for Students of Analytical Chemistry. By CHARLES J. MOORE, PH.D. (VIRGINIA), Austin Teaching Fellow in Advanced Analytical Chemistry in Harvard University. Boston, New York, Chicago, London: Ginn & Company. pp. viii + 78. Price, $1.00.

This useful little book contains 28 tables of the numerical constants and factors most frequently made use of in analytical chemistry, together with the corresponding logarithms. A six-place table of logarithms is also given, followed by brief explanatory directions for the use of the various tables. The type is exceptionally clear and this little book should prove very useful. C. A. R.

SPECIAL ANNOUNCEMENT

By an agreement with the Directors of the American Chemical Society, THIS JOURNAL will be discontinued as a separate publication on the completion of the 50th volume and, beginning January, 1914, will be incorporated with the Journal of the Society. A fuller statement in regard to the consolidation will appear in the December number.